



AGRICULTURAL RESEARCH INSTITUTE  
PUSA

---





THE JOURNAL  
*of the*  
TEXTILE INSTITUTE

VOL. XXXII—1941

PROCEEDINGS AND INDEX





# THE JOURNAL OF THE TEXTILE INSTITUTE

Vol. XXXII

FEBRUARY 1941

No. 2

## PROCEEDINGS

### THE SPINNING OF DYED AND BLEACHED YARNS

By DR G ULLMANN, Technical Adviser (Manchester)

#### ABSTRACT

The spinning of bleached and dyed cotton and mixtures of cotton and staple fibre on machines with three lines of rollers has been practised for some years in many countries and increasingly developed

The present article describes the steps of bleaching, dyeing and spinning involved in this rather complicated branch of yarn production, indicates the types of goods for which the yarns are to be chiefly recommended, and discusses questions of cost.

The methods under review were for the most part developed by the author himself or with his collaboration

#### INTRODUCTION

In spite of present critical conditions in the world, a brief review of developments in textiles during the past 20 years will inspire optimism. The consumption of textile fibres has been roughly doubled; though the crops of American cotton are as large as they were before the first World War, the share of American cotton in the total crop has fallen from 80 per cent. to below 50 per cent., and the extra cotton has been consumed in spite of the phenomenal growth of artificial fibres. Yarns and fabrics for wear have tended to become finer and lighter, requiring more spindles, looms and knitting machines. The number of consumers of textiles in the world has greatly increased and the demand is for more and more variety in fabrics—in colour, texture, design and so forth.

In order to satisfy the wide popular demand for variety the methods of production must be the cheapest possible. Thus, in many countries printing has had a great vogue, but there are many advantages in coloured woven fabrics, and methods for producing them cheaply but in manifold variety are highly important.

The use of yarn spun from coloured or bleached fibre offers many possibilities in this field. The production of these special yarns has seldom been openly

## SPINNING OF COLOURED YARNS

The " spinning of coloured yarns " includes the spinning of bleached or dyed cotton on machines with 3-line roller systems, the spinning of blends of different coloured cottons or dyed and grey cotton, and the production of so-called Jaspé yarns by the doubling of rovings dyed to different shades or by doubling coloured and undyed rovings. For success in this difficult art there must be full co-operation in all stages, that is, the bleaching and dyeing must be considered as integral parts of the spinning process, just as carding and drafting are.

The spinning machine makes an almost inexorable demand on the physical properties of the fibre and in learning to spin coloured cotton a whole range of factors that influence spinning will be disclosed. First and foremost is the basic fact that *spinning is influenced by the surface properties of the fibre*.

It is well-known that different types of cotton have different surface properties, some, like Indian cotton, are rough, others smooth, and some almost greasy, like certain " exotics " before methods of cultivation were properly understood. Some spinners have learnt how to secure the right surface effects by blending different cottons. The surface effects are displayed in the clinging of the fibres and their behaviour in drafting. In spinning coloured cotton it is soon realised that a very small percentage of cotton of a particular surface property in a mixture is sufficient to improve or lessen the quality of the spun yarn. If the surface property is right, a small proportion of fibre can be quickly mingled with the bulk and impart its properties to the mixture. For the same reason a very light marl yarn which is used in large quantities for the manufacture of a cheap but pleasing knitted fabric can be made with only 3.5 per cent of dyed fibre, the blending is quickly done, usually on the drawframe.

It is because of its normally rougher surface that Indian cotton, in spite of its shorter staple, can be spun, even with less twist, to yarns of the same strength as longer but smoother cottons.

In the early days when wood extracts, mordant colours, and especially basic dyes on tannin-metal mordant were more widely used, it was a common experience that dyed cotton could be spun with 20-30 per cent fewer turns than the same cotton in the grey, because the surface of the dyed fibre was rougher. On the other hand, cotton dyed by a process that involved oiling (e.g. Paranitriline red, Turkey red, and Naphtol colours) or by a process that required a strongly alkaline bath (e.g. Indigo) became so smooth that it was almost impossible to spin it. A similar inconvenience is encountered with staple fibre, especially when treated with a softener, and all the devices proposed by manufacturers for imparting curl to the fibre or impressing it with small furrows are not sufficient means of imitating the surface properties of cotton. For this reason spinners find it easier to spin staple fibre when mixed with a certain proportion of cotton.

Many years ago the author discovered how to overcome such troubles by blending with the mass a small amount of a smoother or rougher fibre, as required, taking advantage of the fact that such an admixture can be rapidly incorporated with the bulk so as to influence the whole mass. The experiences gained in spinning tannin-mordanted dyed sliver—which was too harsh and rough—and Para-red dyed fibre—which was too smooth—when combined led to a solution of the problem which was published in 1923<sup>1</sup>. Oiled cotton was given in the dyehouse a final treatment with weak tannin or other liquors to impart a harsh surface, and the harsh tannin-mordanted cotton was given a final oiling treatment.

The importance of the surface properties of the cotton is demonstrated further by the fact that the author has not been able to spin mercerised cotton. The removal of the cuticle renders the fibre so smooth that no impregnation of

<sup>1</sup> Melland's *Textilberichte*, 1923, 4, 480

the above kind to make a harsh surface was successful. It was not intended, of course, to produce a lustrous yarn by spinning loose mercerised cotton, but it was hoped by this means to secure a stronger yarn and to obtain the two-tone Jaspé effect by twisting together mercerised and unmercerised cottons in the form of rovings.

The two-tone effect can obviously be secured by combining rovings of grey cotton and acetate staple fibre and then dyeing the yarn. It is advisable, however, to tint one component with a fugitive colour so as to secure visual control of the blending and spinning.

The modification of the surface of a small part of the mixing can also be utilised to good purpose in the spinning of grey yarn containing waste. Spinable wastes, such as strippings, fly, combings, good types of scutcher droppings, etc., are frequently subjected to a wet treatment for the removal of woody material and fatty matter, and also in order to improve the colour. It is then a simple matter to end this wet treatment with a suitable impregnation of the fibre so as to modify its surface.

Mention may also be made of the spinning of mixtures of cotton or staple fibre with wool, a trade that has been practised in this country for several years and has recently been developed for mass production abroad. The yarns are chiefly used for knitted fabrics and a very small percentage of wool is sufficient to modify profoundly the character of the yarn. In condenser yarns as little as 3 per cent. of wool imparts a woolly feel. The wool appears to be bound in the yarn to great advantage, the ends of the fibres coming to the surface. Similarly with 3-line spinning, a small percentage of wool is capable of conferring on the yarn the handle of wool and of making various cross-dyeing effects possible. If the percentage of wool is increased, say to 20-25 per cent., much more remarkable effects are possible, especially if the fabric is slightly raised.

### PRACTICAL CONSIDERATIONS

The discussion of the coloured spinning process will now be pursued under the headings (1) Dyeing and bleaching, (2) Spinning, (3) Fabrics, for which the yarns are specially recommended, and (4) Questions of cost.

#### **Dyeing and Bleaching**

Dyeing and bleaching may be conducted on the loose cotton, after cleaning by passage through, say, a Crighton opener and possibly a scutcher. The wet processes are carried out in the well-known package apparatus which, though economical to run, is not elastic enough for a sequence of process stages such as are demanded by the newer fast dyes. Alternatively, the processes can be applied to sliver, either compressed in cans containing 4 or 5 lb each, or after the fashion in which combed wool is usually dyed.

A very good continuous machine for bleaching and dyeing sliver—due to Mattei—has been in use for a long time. For reasons of patent licences it has never been advertised much nor widely introduced, whilst developments have been kept secret. The apparatus gives very good results and makes possible the use of difficult dyes such as Indigo, the Naphtols and dyes that require more than one stage.

In a newer method, already working satisfactorily in many mills abroad, the slivers are wound on perforated beams and treated in beam-dyeing and bleaching apparatus.

Rovings may also be dyed on perforated tubes, like cheeses, when spinning very small lots, but this entails the sacrifice of the main advantages of coloured spinning. Dyeing the cotton in a looser form offers more freedom, because the subsequent blending to a uniform shade is easier, and there is still the possibility of mechanically cleaning the stock and loosening bundles of fibre, that may have been matted together by lime soap or oil residues or entangled in the wet

processes. An attempt was made to put extra twist into rovings, wind them into hanks, dye them in this form and then remove twist and wind into slubbing bobbins, but without success.

It remains, therefore, that for most purposes, except perhaps where very large quantities are to be spun to the same shade and count, the spinner is well advised to carry out bleaching and dyeing on the sliver. The blowing room thus handles grey cotton only, the wastes remain undyed and retain their full value, and there is no risk of mixing grey and coloured wastes. If, however, cotton dyed loose must be processed, it is advisable to use separate scutchers each fitted with a separate exhaust and dust collecting system of the hose type.

Dyeing of slivers also implies much less waste of dye on mechanical impurities, and in fact the advantages more than outweigh the extra cost of plant and operation compared with the simple processing of loose stock. Since the spun yarn is sold by weight, however, care must be taken to avoid excessive loss of weight in wet processing. In the author's experience there is little hope of making up this loss by any kind of weighting of the fibre, the surface properties of the fibre and its elasticity, hygroscopicity and so forth were adversely affected and in drafting the weighted material the engraved rollers were worn smooth. The loss of weight must be accepted, but in bleaching it need not exceed about 3 or 4 per cent, and in dyeing it would be slightly less. Even with staple fibre there may be some loss due to removal of softener. In spinning to the same counts, therefore, bleached and dyed materials will have more fibres per cross section than grey yarns, and thus be stronger. The buyer should therefore be recommended to purchase dyed or bleached spun yarn in a count some 2-4 per cent. finer than for grey cotton.

Drying requires care to ensure that no portions remain partly wet since this would entail "felting" on the spinning machine and the formation of slubs that are almost impossible to remove. On the other hand, the dried-fibre must be conditioned before spinning, which is best secured by storage in a damp cellar for a few days or by treatment with moist but drop-free air in a room or machine at the correct temperature.

It is essential that the fibre should be allowed to rest for some time before spinning so that it may recover from the stresses imposed during bleaching and dyeing. Sometimes it is desirable to apply an after-treatment with a softener and it is also useful to impregnate the fibre with a small quantity of a hygroscopic substance, such as common salt, to hasten the regain of moisture.

Extraneous impurities, such as oil spots, must be carefully watched and the water supply must be considered since impurities that bind the fibres together, for example lime soaps from hard water, cause much inconvenience in spinning.

One advantage to the dyer is that he is not compelled from the outset to dye to shade. He can continue dyeing without interruption, correcting his recipe in later batches, since the required shade can be secured by blending different lots. Naturally, they should not differ too widely in shade.

Some practical hints may now be given. It must be emphasised again that dyeing must be considered in relation to the spinning and excessive loss of weight and of the natural fat and wax avoided. Thus, the wetting out and dye liquors should not be too hot, previous wetting out is particularly recommended for sliver dyeing, and it may be said that wetting agents are often effective in much smaller quantities than those generally used. Further, since most of the liquors used are alkaline—and the alkalinity is high for fast colours—the fibre must be well covered with liquor to exclude the air and thus avoid formation of oxycellulose. Such attack on the fibre leads to dust in spinning and reduces the strength of the yarn. If alkaline baths must be used it is better to employ mixtures of caustic soda and soda ash than caustic soda alone.

With appropriate wetting out and measures for removing impurities it is possible to utilise cotton that is off colour, spotted, stained, damaged by sea

water or water used to extinguish fire, or even mildewed. Comparatively dirty waste can also be transformed into a cheap, useful material. Such stained cotton will naturally be reserved for dark shades—black, brown, navy blue and so forth.

"Dead cotton" causes many difficulties and this is a further reason for preferring to dye in the sliver form, after the opening and carding have eliminated it as much as possible. Dead cotton occurs in the raw material in clots but dyeing breaks these up into small parts that are dispersed throughout the mixing, forming most undesirable neps. There is a way to cover dead cotton, but unfortunately it can seldom be used. It consists in using a relatively high concentration of dye, which necessitates a very small ratio of fibre to liquor. This is possible with continuous processes, especially with the Mattei sliver dyeing machine, but not with the ordinary package dyeing apparatus. Sometimes it is possible to start the dyeing operation with the concentrated liquor and after a few minutes to add the required volume of water to secure the right ratio.

Loose cotton and slivers take more dye than yarn in hank form, and this more than yarn on cheeses or beams. The penetration is more complete, and for the same reason spun dyed yarn is usually duller than hank dyed yarn.

This dullness is a drawback in some shades, notably red, but it is possible to improve matters by what may be called an "optical" way. The dyer and user of Turkey red yarn are aware that much of the brilliance is due to the fact that the dye is mainly deposited on the exterior and that a paler shade is obtained by re-twisting the yarn so that the core is exposed. Indigo dyed yarn presents the same effect. This phenomenon can be imitated in spun dyed yarn by blending with the stock a small quantity of much paler fibre. The eye has very little analytical power of distinguishing individual fibres, being mainly responsive to the total optical impression, and the admixture of the paler fibre relieves the dullness of the main bulk.

Useful economies are possible by the use of old dye baths, even when they differ somewhat in shade, because the correct shade of the yarn can be secured by blending the stock. Similarly, it is possible to work up surplus stock; for example, one residual sliver may be doubled on the drawframe with five or six slivers of a new batch.

Drying should not be carried out at too high a temperature because of the difficulty of reconditioning the material and because of the effect on any hydro-cellulose or oxycellulose that may have been formed. Continuous drying machines are available in which the sliver is treated roughly like a warp in an air-drying tape frame, and in the latest models the sliver is coiled down in cans at the outlet. Special care must be given in this case to the reconditioning.

If the drying is not continuous and carried out on the compressed sliver, a string is run through the coils and hung up in the drying chamber with the coils riding loose and freely exposed to the air. It is then possible to send a current of cold, moist, but drop-free, air through the chamber to start the reconditioning of the dry sliver. The processes can be carried out without producing dust or fly, so that it is possible to spin different "shades" side by side on the same frame, with the same draft. It is inadvisable, however, to spin very dark shades together with pale shades, or grey or bleached yarn, partly because of the cleanliness of the operative's hands.

### **Spinning**

It has been explained above why it is preferable to carry out bleaching and dyeing on slivers. When, however, large quantities are to be processed in the same shade, or blendings are to be made for knitted fabrics of the Jaeger type, containing not more than about 10 per cent. of lightly dyed fibre, then it may be preferred to dye the cotton in the loose. In this event, part of the blowing

room, including the scutcher, should be isolated and the dyed waste not allowed to mix with the grey waste in the dust chambers. The cotton is usually processed as far as the first scutcher lap before dyeing, in order to remove most of the dust and trash and thus economise on dyestuffs.

For dyeing in the sliver form, "double carding" may sometimes be recommended, each carding being very light. The first carding should result in sliver of hank number about 0.08, the flats running at a low speed so that only the gross impurities are removed and the waste is less than normal. The coarse sliver is then dyed or bleached, combined on a Derby doubler and carded a second time to give the usual sliver, say hank-number 0.12 or 0.13 for medium coarse counts. The rate of production may be raised in the first carding to 180 lb per 8 hours, and in the second carding to, say, 120 lb. The setting of the grid bars and the speed of the flats are changed so that the total waste is not appreciably larger than in single carding. The increased cost for wages is not important, but naturally more cards are required.

Dyed sliver from the second carding is in the best form for feeding to the drawframes, but sliver direct from bleaching or dyeing often requires extra assistance in the drawing process. One method is to use a device after the pattern of a gill box to loosen tangled fibre.

Furthermore, the slivers are frequently broken so that normal production is impossible at the first drawing. To overcome this difficulty, the first drawing should have more heads or an auxiliary drawframe might be used to prepare the sliver for the normal drawing. It is also urgently necessary to secure that fibres that are stuck together in bundles or felted together in the dyeing and bleaching are completely separated. To this end, the first line of rollers may be of the loose-boss type. The first drawing should not be hurried, drawing is cheap work and extra care at this stage is amply repaid. Special cleanliness should be observed.

Advantage may be taken of the surface properties of the fibre by treating the leather cots so as to obtain a better grip. They may be coated with an alcoholic solution of sodium silicate which on evaporation of the spirit leaves the leather rougher. The grip is thus improved and bundles of fibre are opened better. On the other hand in order to make the leather cots smoother, the spinner can treat the cots with feather alum.

The complete isolation of the fibres is of paramount importance for the further treatment, especially when high-draft systems are used. High-drafting is particularly advantageous in spinning dyed cotton for it offers extra latitude to cope with irregularity of staple—due, say, to damage in bleaching and dyeing, and provides the opportunity to work in dyed waste or small remainders of dyed cotton.

The blending of slivers of different shade according to any desired plan can readily be carried out at the first drawing, but this requires sufficient floor space for the cans. Certain types of "melange" yarns are also made by combining one or more dyed slivers with grey slivers but special care must be taken to maintain the feed of the sliver in the correct proportion. The drawing must not be hurried and it is advisable to use more heads at the first drawing. It is also possible to mix in at the first drawframe wool or certain types of staple fibre. Furthermore, wastes can be introduced by combining one sliver of waste with five or six slivers of fresh material.

This consideration of the utilisation of waste raises two questions of the greatest importance for the economics of the spinning of coloured cotton. One is the size of the single batch, and this will be discussed later. As spinning is based on mass production there must not be too many interruptions through having the single batches too small. The second question is the best way of using the wastes. Being dyed, they have consumed dyestuffs, chemicals, steam,

power, wages and overhead expenses, but in small lots they may be worth only half as much as grey wastes of the same type

If very large lots are to be spun continuously or repeatedly in the same shade—black, navy blue, brown or khaki, and also bleached—the problem is readily solved by returning the loose waste to the blowroom, preparing a sliver and combining it with other slivers on the first drawframe

For smaller lots in special shades or of special qualities we introduced some years ago a method of dealing with the waste that proved most economical and has been adopted by other mills. We installed waste cards (roller cards) arranged with coiler motion and automatic weighing motion with which quite small quantities of spinnable wastes could be converted into slivers just as they came from the machines, and these slivers were suitably blended with other slivers at the drawframe, leaving only a relatively small proportion of the waste to be stored. This material was either compressed in sliver cans or cross-wound and reserved for a subsequent batch in the same or similar shade. The fact that a uniform result can be obtained by mixing different shades helps in the disposal of the waste

The mill manager should have a sample collection, brought up to date each day, so that he can see what wastes or surplus he has in stock and arrange to absorb them as soon as possible.

Much trouble is caused in spinning if the dyes are not fast to rubbing. The dyer should give a thorough rinsing, and avoid deposits of lime soap, putting too much dye on the fibre, using too much salt in the dyebath, and other factors that cause the dye to be deposited mainly on the surface. The same kind of trouble is encountered with sulphur blacks, which are prone to "bronzing". Some dyes, such as a few of the Naphtols, are habitually not fast to rubbing. Other dyes that have lost some of their former importance, such as indigo and aniline black, have the same defect. Turkey red, made by a simple process, gives the same trouble.

In spite of all precautions it often happens that the leather cots of the drafting rollers show traces of the dye rubbed off from the cotton and other material processed on the same drawframe tends to be tinged by it. The only remedy the author could find was to keep special spare top rollers for such shades as Naphtol reds, unless the machines could be kept continuously on one colour. The trouble is encountered mainly at the drawframes and the spare rollers are kept for the first or first and second machines.

If the slivers are properly prepared and drafted so that the individual fibres are well isolated there should not be any difficulty on the slubbing, intermediate, roving and spinning machines, much depends on the correct re-conditioning of the dyed or bleached fibre.

There are, however, some difficulties for which the spinning department is responsible. A few of them are not confined to the dyed or bleached material, with which they are readily observed, but are encountered also with grey yarns and give rise subsequently to trouble in bleaching and dyeing—that is usually not correctly diagnosed. For example, if the wooden bobbins—or even papier maché or other bobbins—used on the speed frames have small cracks, oil may penetrate from the spindle to the fibre. This shows on dyed material as a dark ring and on bleached material as a yellow, shining ring and the final thread may be stained for a few hundred yards. Basic colours on tannin mordants absorb this oil particularly avidly, and it was this observation that led the author to give basic colours a final treatment with a dispersed oil and to remove excess of oil from fibre that had received oil in dyeing by treatment with tannin. The favourable effect on the surface properties, which at once made it possible to spin difficult material, has already been emphasised. It is important, therefore, that the bobbins should be free from cracks.



In order to avoid piecing marks, the operatives should have clean hands and provision should be made near the machines for them to wash frequently with soap and warm water. Furthermore, operatives should be selected for piecing who do not suffer from perspiring hands. In some mills operatives rub feather alum into their hands and fingers to absorb perspiration but it is better to avoid this.

This leads to a discussion of the influence of temperature and humidity. The best temperature for cotton spinning is about 26-28° C. (79-82° F). For carding, a relative humidity of about 60 per cent is best and for spinning cotton on mules or ring frames about 70-75 per cent. Staple fibre requires a higher humidity, and about 90 per cent is recommended for spinning, an intermediate value might be adopted for mixtures of staple fibre and cotton.

The degree of humidity has a very big influence on the cleaning of cotton in the blow-room. Some spinners think it to be unnecessary to store cotton after opening the bales, but others, including the author, prefer to hold the opened cotton in mixing bins for five days or so, the bins being isolated to reduce the risk of damage by fire or water. Artificial humidification in the blow-room is usually unnecessary, the best conditions being only 50-55 per cent R.H. at about 80° F. In the author's experience it is only for a very few days in the year, except in Tropical or Southern Continental countries, that artificial humidification is required.

Dry cotton is easier to clean than moist cotton and this experience has led to a method for diminishing the trouble of "dead" cotton. This trouble was most acute in the production of a very profitable line, namely, marl yarns from dyed and a few grey fibres for knitted fabrics, imitation woollen fabrics or half-wool clothing fabrics. Formerly it was necessary to use the very cleanest and best cottons and to resort to double or even treble carding, especially for the darkest—and most in demand—shades with only 10 per cent or less of grey fibre. Alternatively, very carefully combed cotton was required, and by such means very clean but expensive yarns, almost free from nep, were produced, especially in France, Switzerland, Poland, etc. Contrary to all precedent, however, the author installed a drying machine in the blowroom, heated the cotton to about 70° C. (158° F) and passed the hot cotton through the Crighton opener and scutchers with the grid bars set closer than usual. Production was not high but the cotton was clean and offered the possibility of using much cheaper cotton than usual. The waste from this hot-cleaned cotton could be utilised in ordinary yarns without difficulty.

Conditioning of dyed spun yarns also needs special care. The crude method of immersion in skips is absolutely inadmissible and not even spraying with a definite amount of water containing a wetting agent may be used. Certain dyes are inclined to "spot" when the locally over-wetted yarn is stored in cases. The only advisable methods are the old-fashioned cellar conditioning or a mechanical imitation of it in which drop-free moist air is passed through the yarn. Local over-wetting of dyed and, especially, bleached yarn must be avoided also because dirt tends to adhere easily at these places.

#### **Fabrics for which Bleached or Dyed Spun Yarns are specially suitable.**

By comparison with dyeing yarn in hanks, beams or cheeses, dyed or bleached spun yarn offers great advantages in fine weft counts since one process of winding is saved. Dyed spun yarn can be utilised in shuttles directly, with saving not only in wages but in purning waste. Yarn for doubling or twisting offers the same scope for the saving of winding costs. The monetary advantage should be considered in relation to the extra cost of production of the dyed spun yarn.

Dyed spun yarns are preferred for certain cloths that could also be produced from beam- or cheese-dyed yarn when a perfectly level shade is required and

particularly when the fibre must be evenly penetrated through and through. This is the case, for example, with army uniform cloth, to avoid the development of light patches where the rifle belt and the like cause rubbing.

The production of a large bulk of fabric completely level in shade is more readily achieved with dyed spun yarn. This is of considerable interest in the production of certain knitted fabrics where the optical effect depends on the shade of the one yarn.

The levelness of the bulk is also of great advantage in weaving on change-box looms, the optical effect will always be the same even though many different shades of weft are used and patterning possibilities are wider than when coloured warps only are used. It is a question for individual consideration whether it is also advantageous to use dyed spun yarn for warp. Variations in shade in beam dyeing can be readily marked by careful mixing of dyed beams, but when the same shade is used for warp and weft, as in checks, it is often better to spin the warp and weft from the same dyed material, especially for small lots. The advantage is greatest in the weaving of light fabrics with fine-count weft.

Dyed spun yarn can be used for weft or knitting in the softest twists so that the fabric is softer and of fuller handle.

The monopoly field for dyed spun yarn is naturally that where the yarn is spun from blends of cotton of different shades. First and foremost are the melange yarns which are consumed in large quantities in the knitting industry and, especially in half-wool or cotton fabrics, for clothing.

Another variety of spun yarn for which different shades are used is the so-called Jaspé yarn, which though single gives the impression of two-fold yarn. This is because on the flyer or spinning frames two different rovings are twisted together, such as coloured/grey, coloured/bleached or coloured/coloured. The appearance of the yarn is more hazy if the Jaspé yarn is made as "flyer Jaspé" because the drafting effects some marl-like mixing. Even with mule or ring frame Jaspé, however, where two fine rovings are combined, the appearance is rather less sharp than with true doubled yarn. The difference can be very much reduced if the roving is made a little finer than for single dyed or grey yarn so that the draft is smaller. An "optical" correction is also possible by having the darker roving rather coarser than the lighter component, say in the ratio 55:45.

For some articles, particularly some clothing fabrics, the hazy appearance is preferred, and here very interesting effects can be secured if the Jaspé yarns are made from melange rovings rather than plain-dyed and undyed rovings. The author has produced a cotton yarn in large quantities for uniforms that closely imitated the same type of cloth woven from wool melanges, so that a summer uniform made only of cotton was very similar to the winter uniform made of wool. Similarly, the so-called "insular effect" characteristic of some wool melanges—the dye being concentrated in certain parts—could also be obtained in cotton, giving a very pleasing cloth that wore well and did not readily show dirt marks.

By means of Jaspé yarns for weft or warp and weft it is possible to replace effectively fabrics that are usually made from doubled yarns. Such cloths have been used in large quantities in some countries for railway porters' uniforms, school uniforms, sports clothes and workmen's suits. For example, the railway surting usually woven in warp and weft from 2/24's, one thread blue and the other grey or bleached, or black and white, was imitated by using as weft a black and white Jaspé yarn, 12's-14's, or slightly heavier Jaspé yarns for both warp and weft, in order to get the required strength. In the latter case, the Jaspé yarn was produced on the spinning frame, but for certain other fabrics, especially knitted ones, "flyer Jaspé" was preferred. Jaspé yarn and blended yarns, but especially Jaspé yarns made from blended rovings, allow the manu-

facture of very interesting and very attractive fabrics which are raised on one or both sides. Cloths very much resembling woollen fabrics can be made in this way and more effects are obtained by using yarns containing staple fibres.

Dyed spun yarns, particularly in fine counts, have also found wide interest among manufacturers of poplins, zephyrs, curtain materials, ties, umbrella cloths (especially with silk or rayon warp) and handkerchiefs with coloured parts for which piece bleaching was not advisable.

For such articles, but also for other specialities, very good use can be made of yarn which is made from partially bleached cotton, so that by chemicking with chlorine or peroxide without any boiling process a very good white can be obtained. Such yarns are very cheap to manufacture, but they command a good price, because they simplify the manufacture of coloured woven fabrics and also fabrics containing more rayon for instance in the warp or weft. Otherwise it would be necessary to bleach such mixed fabrics so strongly that the cotton would be fully bleached, which cannot otherwise be done without affecting the dyes or the rayon or staple fibre part. Thus a cheaper method of manufacture of such fabrics is possible.

### Questions of Cost

The difference in production costs between spinning coloured yarns and dyeing grey yarns concerns spinning as well as dyeing. Dyeing and bleaching of the loose cotton or sliver require simpler apparatus than for yarn dyeing and the wage cost is lower, but the consumption of dyes is somewhat higher. More free space is required in the dyehouse for blending the different shades and more storage space must be available to cope with remainders and the spinnable wastes.

The chief objection by the spinner, however, is the frequency with which shades and qualities have to be changed, so that production is not so continuous as in grey spinning. Except for spinning bleached cotton and yarns for uniform cloths, it seldom happens that very large batches are worked up in the same shade and quality.

This difficulty can be reduced by "spinning in roads", a few flyer spindles are used for a certain shade—say 20 spindles on the roving frame—leading up to, say, 200 spindles on the mule or ring frame. This presupposes that the different shades on the one frame are to be spun to the same twist and count. It can be arranged that there is no fear of "fly" from one shade being deposited in the neighbouring "street".

This necessitates, however, sufficient free space for assembling the various shades before spinning begins and for collecting the different yarns. More machines are also required than for grey yarns. Mention has already been made of the need for more drawframes, it is also advisable to have more cards, including roller cards with cooler motion, and a doubler for double carding.

The number of operatives required is not larger than for grey spinning, but more cleaning and storing are necessary.

It is not easy to say what is the smallest quantity that can be spun economically, but 500 lb may be regarded as a working figure for medium counts. If smaller lots are called for, the spinning costs are higher. In higher counts, the saving of winding costs is to the advantage of the buyer. For very small lots, it may be desirable to dye rovings in apparatus like that for cheeses, but this sacrifices some of the advantages of dyed spun yarns and the dyeing apparatus and operation are more costly.

It is as well not to allow the buyer too much freedom in the choice of shades and rejection of imperfect matches. He might be asked to control the irregularities in shade against which he does not complain when buying yarn.

dyed on beams, cheeses or hanks<sup>1</sup> In actual fact, a coloured yarn spinner when supplying the same shade in repeat orders can guarantee a match more easily than the yarn dyer.

It is useful to supply sample cards and to allow the buyer some latitude in ordering smaller lots from these normal shades If he demands a different shade, however, the order should be accepted only for a large lot, say 1,500 to 2,000 lb for delivery in one batch, or for delivery spread over a few months, otherwise an adequate increase in price must be charged

One source of profit in dyed spinning is the possibility of using cheaper types of cotton such as the brownish Coconadas and Westerns, spotted and stained cotton, and even cotton that has been damaged by sea water or mildew Such "off-colour" cottons can often be obtained cheaply and can be utilised for many shades They should be of good staple and strength, however, and above all reasonably free from dead cotton

The mill should be kept busy and, therefore, should not be too large A single plant with more than 60,000-80,000 spindles would not be suitable except when on large bulks of the same shade and count, or on bleached cotton The mill should have its own bleaching and dyeing plant But a beginning could be made by commission dyeing provided that effective collaboration with the dyer is secured.

The technical management should be in the hands of a man who understands bleaching and dyeing as well as spinning, but relies on assistants to control the individual operations He should also be in personal contact with buyers and should study the uses of these special yarns so as to advise his customers about new developments It is therefore useful even for a spinning mill that sells its production to have a weaving shed in which to absorb surplus yarn and to experiment on new fabrics. These would be shown to customers with particulars of their construction so that a demand could be created for the yarns

Thus it is seen that coloured and dyed spun yarns offer many manufacturing possibilities for the home and export markets in coloured woven or knitted fabrics and fancy yarns The special effects are obtained cheaply Spun coloured yarns should prove of great value in the export trade since it is extremely unlikely that continental countries will be able to manufacture them in the near future As the varieties of such yarn are so numerous the demand for these products should be great In the countries in which this type of trade was developed the production reached very high figures and the present time seems favourable for British spinners to enter this market. The process of manufacture is specialized and to the technical man the production of dyed bleached spun yarns presents a new opportunity

The author wishes to express his best thanks to Dr J C Withers for his kindness in connection with the preparation of this paper.

## NOTES AND ANNOUNCEMENTS

### Annual General Meeting, 1941

Arrangements are being made to hold the Annual General Meeting of the Institute on Wednesday, 23rd April. Details of the time and place of the meeting will be issued to members later.

### Council Vacancies, 1941

In accordance with the Bye-laws ten of the thirty members of Council retire each year. The names of the present members and the years in which they are due to retire are shown in the following lists.

1941	1942	1943
J Chamberlain	H Bromley	H C Barnes
J E Dalton	W B Crompton	F Chadwick
J R S Goodall	J Day	W Davis
H G Greg	N C Gee	H Greenwood
G Haigh	F C Harwood	W Howarth
R Lord	F Kendall	W E King
W E Morton	S Kershaw	H Nisbet
H Richardson	J Read	W Pritchard
J. B. Speakman	F P Slater	A W. Stevenson
G H Thompson	J C Wrthers	W Wilkinson

Election takes place at the Annual Meeting, and nomination forms are being supplied to all members of the Institute so that nomination for the ten vacancies occurring in 1941 may be made.

### Examinations 1941

Members who have applied for Associateship of the Institute and who have been referred to the examinations should note the following dates —

Preliminary Examination	21st May
Examination in General Textile Technology	28th May

Those applicants who wish to be candidates at either or both of these Examinations would assist by completing the appropriate entry forms as early as possible. The final date for notification of entry is 14th April.

## Lancashire Section

The Committee has decided to hold the Section Annual Meeting at the Institute's premises on Saturday, 22nd March, instead of having an evening meeting as was previously arranged. A lecture will follow the business part of the meeting and will be given by Mr H. Rostron on "Selection and Training of Textile Operatives."

## General Items

Elections to Fellowship and Associateship have been completed as follows, since the appearance of the previous list (January issue of the *Journal*):—

### FELLOWSHIPS

- HUBERT CONRAD WALTER, Esq, M A, LL B, F C I.S.,  
Managing Director, Morgan Crossley & Co Ltd., Manchester  
BERNARD PAUL ROTHWELL, Esq, M Sc (Vict),  
Technical Adviser, Ashenhurst Dyeing Co Ltd, Blackley, Manchester  
GEORGE ALBERT RUSHTON, Esq, F R S A, A.T.I.,  
Inspector of Textile Stores, Office of High Commissioner for India, London  
HARRY AUGUSTUS TURTON, Esq,  
Retired General Processing Manager, Courtaulds Ltd., Foleshill.

### ASSOCIATESHIPS

- JAMES ROUSE, Esq  
JOHN EMERSON PRIESTLEY, Esq  
NRIPENDRA NATH BASU, Esq.  
CLARENCE NORCLIFFE, Esq  
AHMED SELIM, Esq.

### Institute Membership

At the January meeting of Council the following were elected to membership.—

#### *Ordinary*

- A S Gilhes, 12, Regent Park, Tollygunge, P O, Calcutta (Manager, Technological Research Laboratories, Indian Central Jute Committee)  
H de G Gaudin, The British Northrop Loom Co, Ltd, Blackburn (Director and Sales Manager)  
J S Henshaw, 62, St John's Road, Ilkeston, Derbyshire (Textile Tester and Assistant Manager in Finishing Dept)  
H A. Swift, 59, Piccadilly, Manchester (Fabric Producer).  
H Sneyd, 132, Crossbank Street, Oldham (Woollen Spinner, Research Dept, Arrow Mill, Courtaulds Ltd, Rochdale)  
R F York, 401, Syston Road, Thurmaston, Leics. (Foreman Dyer—Hosiery)

#### *Junior*

- A Brearley, 43, Haugh Shaw Road, Halifax, Yorks. (Stock Manager's Assistant)  
D F Coates, 3, Bank Avenue, Horsforth, Nr. Leeds (Laboratory Assistant of the Dept of Colour Chemistry and Dyeing of the Leeds University).  
S W. Greateorex, 17, Kensington Avenue, Victoria Park, Manchester 14 (Textile Tester, Chamber of Commerce Testing House).  
S Mullock, 213, Errwood Road, Levenshulme, Manchester 19 (Textile Tester, Chamber of Commerce Testing House)  
B Saunders, Station House, Newlay Grove, Horsforth, Leeds (Assistant Dyer, Frederick Wilson & Co Ltd)  
Miss V Waterhouse, 13, Oakwell Drive, Ilkeston, Derbyshire (Designer of Knitted Outerwear)  
B. H Williams, 5, Tabley Grove, Longsight, Manchester (Textile Tester, Chamber of Commerce Testing House).

## Employment Register

The following announcements are taken from entries in our Register of Members whose services are on offer. Employers may obtain full particulars on application.—

- No 217—M.Sc., A.I.C., 31 years of age, desires position as Chemist. Eight years' experience as Chemist in Research Department, also experience as part-time Teacher. Willing to go abroad.
- No 218—Applicant desires position as Assistant Manager or similar responsible position in Woollen Yarn Manufacture. Age 31 years. City & Guilds Full Technological Certificate for Woollen Yarn Manufacture. Fourteen years' experience in Woollen Carding, Spinning and Twisting, also experience in Organising and Departmental Management.
- No 219—A.T.I., 42 years of age, desires responsible position in weaving mill. Twenty-four years' experience as Preparation Manager and Costs Clerk.
- No 220—Young man, 22 years old, desires position as Designer, Textile Tester or Pattern Loom Man. Nottingham University Diploma in Weaving, City and Guilds Certificate in Textile Testing and Cloth Analysis. Matriculation.
- No. 221—A.T.I., 36 years old, desires position as Cotton or Worsted Spinning Mill Manager or similar position. Six years' experience as Cotton and Worsted Mill Manager. Evening Lecturer in Cotton Spinning, and Textile Mechanics. Associate of Salford Royal Technical College.
- No 222—A.T.I., 43 years of age, desires position as Manager in Textile Production or Buying. B.Sc. in Colour Chemistry and Dyeing. Twenty years' experience in Carpet Manufacture and buying therefor. Capable of taking charge of plant for Carpet Manufacture.

## Review

**Plastics in Industry.** "Plastes" (pp 241+xii 32 plates and 8 diagrams)  
(London: Chapman & Hall. Price 12/6)

This book is stated to be intended primarily for industrialists seeking new constructional materials. The authors have packed it with up-to-the-minute data on the numerous available plastics, their properties and uses. Even to a person unversed in the intricacies of injection and high pressure moulding and of extrusion methods, the book is eminently readable. The story of modern plastics and their application in such diverse directions as buttons and aircraft, coffins and toys, laminated gears for steel rolling mills and radio sets, is of absorbing interest when told by "Plastes".

It is perhaps unfortunate that the chapter on "Plastics and the Textile Industry" should be so weak. The various synthetic fibres themselves plastics, are briefly described, but the wide and ever-growing field of textile finishing, so comprehensive in its new uses for plastics, is almost ignored. This chapter is also disappointing in its implication that the Textile Industry is lacking in initiative and tolerance toward new developments.

It is hoped that this chapter will be expanded in subsequent editions, with references to recent work in this field.

The work is on the whole well furnished with references to recent publications on plastics, is admirably illustrated and well printed. Apart from the weak textile section, it is an admirable and interesting volume. R. J. SMITH.

## NOTICES: INSTITUTE MEETINGS

- Tuesday, 4th March *Manchester*—1 30 p.m Meeting of the Diplomas Committee at the Institute
- Tuesday, 4th March *Manchester*—2 45 p.m Meeting of the Publications Committee at the Institute
- Wednesday, 5th March *Manchester*—10 30 a.m Meeting of the Drafting Committee—Sub-Committee for Shrinkage Testing Methods, at the Institute
- Wednesday, 19th March *Manchester*—1 30 p.m Meeting of the Finance and General Purposes Committee at the Institute
- Wednesday, 19th March *Manchester*—2 45 p.m Meeting of the Council at the Institute

### LANCASHIRE SECTION

- Saturday 22nd March *Manchester*—2 30 p.m Annual Meeting of the Lancashire Section, to be followed by a lecture, "Selection and Training of Textile Operatives" by H. Roston, Esq. The meeting will take place at the Institute

### MIDLANDS SECTION

- Saturday, 22nd March *Nottingham*—Annual General Meeting Time and place to be arranged

### SCOTTISH SECTION

- Saturday, 15th March Annual General Meeting Time and place to be arranged

### YORKSHIRE SECTION

- Thursday, 20th March *Bradford*—7 0 p.m Lecture "Popular Photography," by R. R. Rawkins, Esq. (Ilford Ltd.), at the Midland Hotel, Bradford. The meeting will take the form of a Ladies' Evening
- Thursday, 27th March *Bradford*—7 0 p.m Annual Meeting of the Yorkshire Section, to be held at the Midland Hotel, Bradford

### OTHER ORGANISATIONS

*Federation of Textile Societies and Kindred Organisations—*

- Saturday, 29th March Meeting of the Committee of Management at 16, St Mary's Parsonage, Manchester 3, at 2 45 p.m

*Blackburn Textile Society—*

- Saturday, 15th March Visit to Blackburn Sewage Works, Samlesbury

- Friday, 21st March *Blackburn*—Lecture "The Microscopy of Textile Fibres," by J. Ranson, Esq., F.G.S., A.M.I.M.E. (Technical College, Blackburn)

*Bradford Textile Society—*

- Monday, 3rd March *Bradford*—7 0 p.m Lecture "Recent Developments in Wool Combing," by A. Geoffrey Peel, Esq. (Messrs. Robinson & Peel Ltd., Bradford), at the Midland Hotel

- Monday, 17th March *Bradford*—7 0 p.m Lecture by H. Holdsworth, Esq., M.P., at the Midland Hotel

- Monday, 31st March *Bradford*—7 0 p.m., at the Midland Hotel—Annual Meeting



*British Association of Managers of Textile Works—*

Saturday, 1st March *Manchester*—Lecture “Synthetic Fibres,” by Dr  
H A. Thomas

*Bury and District Textile Society—*

Friday, 14th March *Bury*—7 30 p m Lecture “Yarns and Fabrics,”  
Exhibition of samples, by H Tonge, Esq ,  
A T I , at the Technical College

Friday, 28th March *Bury*—7.30 p.m Lecture “Fire Precautions in  
Mills,” by W Thomas, Esq , A M I F E  
(Superintendent of the Fire Brigade, Bury), at  
the Technical College

*Dewsbury Textile Society—*

Tuesday, 11th March *Dewsbury*—Lecture “Woollen Rags,” by Bernard  
Hepworth, Esq , Ossett

*Morley and District Textile Society—*

Tuesday, 4th March *Morley*—Lecture “Synthetic Fibres,” by W  
Hardacre, Esq , A T I.

# THE JOURNAL OF THE TEXTILE INSTITUTE

Vol. XXXII

MARCH 1941

No 3

## PROCEEDINGS

### NOTES AND ANNOUNCEMENTS

#### HONORARY SECRETARIES OF REGIONAL SECTIONS —RECOGNITION OF SERVICES

Some time ago the Council decided to show its recognition of the valuable services to the Institute of three Honorary Secretaries who had devoted so much of their time to working for the Sections. It was, therefore, unanimously resolved that a Service Medal should be instituted and the first awards made to Mr A R Down and Mr F J W Shannon, and that Mr A W Blair should be elected to Honorary Life Membership of the Institute. These awards have now been made.

The Council resolved that the Service Medal or Honorary Life Membership should not be awarded unless the period of service was at least ten years. It will be appreciated therefore, that these honours are not lightly bestowed. The Council and members of the Institute are indebted to each one of these members for the strenuous and valuable service which he has rendered. The records of the recipients are as follows.

*Irish Section*—Mr F J W Shannon was the first Honorary Secretary of the Irish Section and held this position from 1926 to 1939. The presentation of the medal was made by the Chairman of the Irish Section, Mr W H Webb, at a meeting held in Belfast on 27th November, 1940. The Chairman testified to the painstaking qualities of Mr Shannon during his long term of office and said it was gratifying to know that his resignation from the Honorary Secretaryship was not due to lack of interest in the affairs of the Institute but to the pressure of business. Mr Shannon expressed his deep appreciation of the honour which had been bestowed upon him by the Institute.

He is a Life Member of the Institute and was elected to Fellowship in 1925.

*London Section*—Mr A R Down became a member of the Institute and was elected to Life Membership in 1923. He acted as Honorary Secretary of the London Section from 1925 to 1940. Mr W H Matthews, Chairman of the London Section, presented the Service Medal on behalf of the Institute at a meeting of the Committee which took place in London on Wednesday, 19th February, 1941. On making the presentation the Chairman said that the

present flourishing condition of the Section was principally due to the initiative and work of Mr Down during his period of office. Mr Down had personally increased the membership and had imbued members with his own enthusiasm for the influential part which a strong Section can play in the affairs of the Textile Institute. When Mr Down found it necessary to resign from office, it had been the wish of all members of the Executive Committee that some recognition should be shown of his services. The Council had expressed its unanimous agreement with this wish by awarding the medal.

Mr Down said that it gave him particular pleasure to receive the Service Medal, and that he greatly appreciated the action of the Council in making the award. In addition he stated that he had always been fortunate in having the full support and assistance of the respective Chairmen and of the individual members of the Committee.

*Scottish Section*—Mr A W Blair joined the Institute in 1925 and has been the Honorary Secretary of the Scottish Section since 1929, he still holds this position. In a section where the members are widely scattered he has worked very hard to bring the members together and to foster the interests of the Institute. The personal contact which he has made with most members in his section and the energy that he has shown in his position as Honorary Secretary have contributed in no small measure to the success which he has achieved in this office. It is gratifying to note that he maintains his activities for the Section and continues to hold office.

## Yorkshire Section

On Thursday, 23rd January, 1941, this section met to listen to papers read by Associates of the Textile Institute. For some years the Yorkshire Section has been accustomed to allot one meeting in each session specially for this purpose. Mr E J Poole of the Wool Industries Research Association covered a wide field in his address on "Problems in Textile Manufacture, with special reference to Woven and Knitted Fabrics". His slides were well chosen to illustrate the points discussed and their exhibition permitted of the necessary brevity in dealing with the many subjects raised in such a paper. An interesting discussion followed.

Mr R Jones, of Shipley, followed with a paper entitled "Textile Calculations Simplified". Mr Jones has made a study of short methods for conversion of counts of yarns, etc., with a view to assisting those who are required to do such things in their daily work. Though most of the methods proposed and demonstrated applied to spinning the author pointed out that they were really of far wider application.

On Thursday, 20th February, 1941, the lecturer was Mr B Ungerson, B Sc., of the National Institute of Industrial Psychology. The subject "Industrial Psychology" was discussed mainly from the point of view of the selection of operatives for work in order to avoid industrial misfits as far as possible. Intelligence tests, tests of reaction time and other psychological "tools" were discussed in a general manner and the lecturer showed how the statistical analysis of observations accumulated in the application of such tests allowed of the proof of the validity of the tests. The occasion deserved far better treatment by the weather, which was appalling, and had a very adverse effect on the attendance.



MR A R DOWN  
Honorary Secretary, London Section,  
1925-1940



MR F J W SHANNON  
Honorary Secretary, Irish Section,  
1926-1939





MR A W BLAIR  
Honorary Secretary, Scottish Section,  
since 1929

## Irish Section

On the 9th January, 1941, Mr D. S. McIlhagger, M Sc , A M I.E.E , of the Belfast Technical College, read a paper on " Humidity Control and Measurement " Measuring instruments and apparatus for the control of atmospheric conditions in test-rooms and workshops were very adequately reviewed and reference was made to special types of apparatus for use in special circumstances

## Reviews

**Rayon & Silk Directory & Buyer's Guide of Great Britain 1940-41.** Published by the Harlequin Press Co Ltd , Manchester Price 21/- net

The compilers of this invaluable directory have naturally experienced to the full extent the difficulties of production in war time In order to compensate for such eventualities as evacuation, since going to press, by firms from their old well-known address for the period of hostilities, the publishers will deal promptly with enquiries sent to Old Colony House, South King Street, Manchester

Manufacturers, Spinners, Dyers, Engineers, etc , are classified in the usual way according to the towns in which they are situated The alphabetical list of firms followed by the names of their towns forms a very useful supplement to this, even though to a certain extent its need is already met by the comprehensive Buyer's Guide

The division of the Buyer's Guide into seven sections is very wise and adds greatly to the value of the directory

Such statistical matter as that presented is mainly of historical interest The practice in some directories of attempting to provide up-to-date statistics is one that inevitably brings disappointment by virtue of the very nature of the publication in which the matter appears In normal times statistics are best handled by the government or semi-government offices and departments specially set up to collect and present the necessary information

The reviewer on receiving such a work, almost automatically begins to test its efficiency by looking up particulars of the firms he knows best or by seeking information with regard to the materials of which he is best informed This directory stands up well to such a test and there can be no adverse opinion regarding its indispensability and usefulness to all engaged, whether fully or partially, in the rayon and silk industries.

**The Cradle and Home of the Hosiery Trade.** Arthur J Pickering, F G S  
(Edited by H W Chandler, Secretary to the Hinckley and District Hosiery Manufacturers' Association )

This book has 156 pages demy 4to, including 35 illustrations, but the last 20 pages, although referred to by number in the list of illustrations, are not numbered There are also 70 pages of well-designed advertisements which are nearly all devoted to the publicity of the excellent products of the Hinckley and District Manufacturers

The book, it is stated, has been compiled " to celebrate the tercentenary of the introduction of the stocking frame into Hinckley by William Iliffe in 1640 A D " This date was several years earlier than the recorded dates of the working of the first frames in Nottingham or Leicester and hence the claim to the " cradle "

The subject matter is arranged in 17 chapters. The history and development of the hand frame and other straight bar bearded needle machines is mentioned in chapters I, II, III, V and VI, and, in addition to quotations from the works mentioned in the bibliography, contains matter and incidents hitherto unpublished, e g a letter from the Revd Thomas Woollen Smith to the late J H Quilter as well as certain comments by Mr Leon Morley.

The rest of the book is mainly devoted to the environment and working conditions appertaining to the local hosiery trade during the period under review, although there is a chapter on "The History of Yarn Production" and another on "The Dyeing of Hosiery".

There is an appendix giving the dates of important inventions, compiled chiefly from Felkin's "History of the Machine-wrought Hosiery and Lace Manufactures" and also a bibliography. These are followed by a number of full-page illustrations of early types of knitting machines and ancient and modern illustrations of the town of Hinckley.

The book gives much information in regard to the development of the hand frame and the social conditions during the growth of the industry in the Hinckley district, but little is said of the critical period between the decline of the use of the hand frame and the successful introduction of the seamless hose machine which initiated the present prosperity of the Hinckley and district hose trade. One would have liked some mention of the struggles of the local manufacturers, in the making of cotton hose on the small loop-wheel heads and the "run-up" ribs, which paved the way to the successful working of the seamless hose machines.

It is interesting to note that on page 41 there is mention of another claimant to the honour of having knitted the first hose made from artificial silk yarn.

The book is well written and its author has worked hard at the literary excavations it involved.

The optimism and enthusiasm shown by the author reflects that of the manufacturers who have also worked hard to give Hinckley its position in the modern, as well as the past, knitting world.

The pen and ink sketches by Miss Cicely Pickering are greatly to be admired being exceedingly interesting and well executed, even if a modern "bottle" bobbin does appear on the ancient hand frame.

One hopes the book will have the circulation it deserves as the descriptions of the times and conditions are not merely applicable to the Hinckley district, but to wheresoever stockings and knitters may have been found.

J C

## NOTICES: INSTITUTE MEETINGS

- Tuesday 1st April *Manchester*—1 30 p m Meeting of Publications Committee at the Institute
- Tuesday 1st April *Manchester*—2 45 p m Meeting of Diplomas Committee at the Institute
- Friday 4th April *Manchester*—1 30 p m Meeting of Committee for Recruitment, Selection of Training for the Textile Industry, at the Institute
- Wednesday 23rd April *Manchester*—11 30 a m Meeting of the Finance and General Purposes Committee at the Institute
- Wednesday 23rd April *Manchester*—2 0 p m Meeting of the Council at the Institute
- Wednesday 23rd April *Manchester*—3 0 p m Annual General Meeting at the Institute

## LANCASHIRE SECTION

- Thursday 3rd April *Bolton*—6 0 p m Lecture "Twistless and Low Twisted Yarns" by A. Draper, Esq., at the Municipal Technical College, Bridgman Place, Bolton

## OTHER ORGANISATIONS

### *Dewsbury Textile Society*

- Tuesday 8th April *Dewsbury*—Annual Meeting

### *Morley and District Textile Society*

- Tuesday 1st April *Morley*—Discussion "Textile Education" Speakers  
A Student, a Textile Teacher and a Textile Manufacturer

- Tuesday 22nd April *Morley*—Annual General Meeting

### *Federation of Textile Societies and Kindred Organisations*

- Saturday 5th April *Manchester*—Meeting of the Committee of Management at 2 45 p m at 16, St Mary's Parsonage, Manchester 3



## General Items

### Institute Membership

At the March meeting of Council the following were elected to membership

#### *Ordinary*

- F Bold, 4, Nab Hill Avenue, Leek, Staffs (Works Manager, Brough Nicholson and Hall Ltd, Leek)
- G Cook-Margett, 9, Barley Cote Grove, Riddlesden, Keighley (Worsted Spinning Overlooker)
- A Haddon, 41, Chalfont Drive, Western Boulevard, Nottingham (Hosiery Works Manager)
- H Henshaw, 13, Blackhills Drive, Ilkeston, Derbyshire (Foreman, Warp Knitting and Raschel Machines)
- F McKenna, 30, Percy Road, Carlisle, Cumberland (Weaving Manager)
- L Morris, B Sc (Tech), A I C, c/o Vantona Textiles Ltd, Ainsworth Mill, Brightmet, Bolton (Textile Chemist)
- W D Rutherford, Heather Mills Co Ltd, Selkirk (Woollen Manufacturer)
- V W Slater, B Sc (Lond), Messrs B Laporte Ltd, Luton, Beds (Research Chemist)
- F R Stafford, M Sc (Tech), A I C, 15, High Crest Avenue, Gatley, Cheadle (Teacher)
- S Swarup, B Sc (Punjab), Kiryu College of Technology, Kiryu, Japan (Research Student)
- F Thomas, 20, Gregory Avenue, Bolton (Head Carder, Mill Hill Spinning Co Ltd, Bolton)
- N Tunstall, 221, Loughborough Road, West Bridgford, Notts (H M I Board of Education)

#### *Junior*

- H Haddon, 41, Chalfont Drive, Western Boulevard, Nottingham (Hosiery Machine Mechanic and Hosiery Student, Nottingham University College)
- S E Sukthanker, B Sc (Bombay), College of Technology, Sackville Street, Manchester (Student)
- H Thornton, 103, Moorend Lane, Dewsbury, Yorks (Assistant Works Manager, Moorend Mills, Dewsbury)

### Employment Register

The following entries appear in our Register of Members whose services are on offer Employers may obtain full particulars on application —

- No 188—Desires position as Works Manager or Chemical Engineer Age 38 years, A T I Experience at home and abroad Production costs and Labour Control Knowledge of Bleaching and Dyeing
- No 222—A T I, 43 years of age, desires position as Manager in Textile Production or Buying B Sc in Colour Chemistry and Dyeing 20 years experience in Carpet Manufacture and buying therefor Capable of taking charge of plant for carpet manufacture
- No 223—Young man, 31 years of age, desires position as Manager in Worsted Spinning 16 years' experience of mill routine in cone and open drawing, flyer and cap spinning 3 years' experience as College Instructor City and Guilds Full Technological Certificate Prepared to take post in British Empire or U S A

# THE JOURNAL OF THE TEXTILE INSTITUTE

Vol. XXXII

MAY 1941

No. 5

## PROCEEDINGS

### NOTES AND ANNOUNCEMENTS

#### COUNCIL'S ANNUAL REPORT AND INSTITUTE ACCOUNTS FOR 1940.

##### 31st ANNUAL GENERAL MEETING

The 31st Annual General Meeting was held at the Institute's headquarters in Manchester on Wednesday, 23rd April, 1941.

The retiring President, Mr H Jaques, A S A A , gave a short resumé of the Institute's activities during the year 1940, as shown in the Annual Report printed below. He closed his remarks by expressing on behalf of the Council and members of the Institute the appreciation of the work done by Mr Frank Nasmith, as Acting Secretary, and by the staff. After the Auditor's Report had been read, the Annual Report and Accounts for 1940 were unanimously adopted.

On the nomination of the Council, Mr G H Thompson, J P , F T I , was unanimously elected as President for the ensuing year. Mr Thompson then took the Chair and expressed his appreciation of the honour conferred upon him. He also took the opportunity of thanking Mr Jaques for his excellent work during a difficult year of office. The Presidential address is given below.

Mr F W Barwick, F T I , Mr J H Bates, J P , F T I , and Mr J H Lester M Sc , F I C , F T I , were re-elected as vice-presidents for a further period of three years.

The Acting Secretary gave the results of the ballot for election to the Council for a period of three years, and the following were declared elected :

J E Dalton, O B E , B A , B Sc  
(Menston-in-Wharfedale)

H G Greg (Manchester)

G Haigh, F T I (Bradford)

R Lord, F T I (Lancaster)

W E Morton, M Sc Tech , F T I  
(Manchester)

F Pickles, F T I (Leeds).

H Richardson, M.Sc. (Bradford)

J B. Speakman, D Sc., F.I.C., F.T.I  
(Leeds)

A J Turner, M A , D.Sc., F.T.I  
(Belfast).

H A Turton, F T I (Coventry)

Messrs Arthur E Piggott, Son, & Co, Incorporated Accountants, were unanimously re-elected as auditors.

The Chairman then declared the meeting closed.

## COUNCIL'S ANNUAL REPORT, BALANCE SHEET AND ACCOUNTS FOR 1940

Presented to the ANNUAL GENERAL MEETING at Manchester,

Wednesday, 23rd April, 1941

### **The Balance Sheet and Accounts**

The accounts as printed show that the finances of the Institute are in a healthy position. It is pleasing to note that members are continuing their support during this difficult period. In view of the excess of income over expenditure it has been possible to write off the previous debit balance and also to make reserves for anticipated increases in expenditure.

### **Policy during the War period**

The policy adopted by the Council has been to maintain to the full those activities of the Institute which are progressive, beneficial and essential, and it can be claimed that the work has been fully maintained. Care, however, has been taken to ensure that time and energy are not wasted on matters which can be well left until after the war. Where possible, meetings are arranged to avoid unnecessary travel and inconvenience, as it is realised that all members are doing their utmost in the country's war effort. The Institute has, on a number of occasions, given assistance to Government Departments, and work of this character is given precedence whenever it arises.

### **Members in His Majesty's Forces**

Notification has been received from about a hundred members that they are now serving in the Forces. The Institute wishes to keep and preserve a full record and would be pleased to receive details from any member who has joined the Forces but has not already notified the fact. Every consideration is given to special conditions which may result from members going on active service.

### **Annual Meeting**

During the previous two years the Annual Meeting has been held away from the Institute's premises. In view of the prevailing conditions, however, the meeting in 1940 was held at the Institute, and no special function was held in conjunction with the business meeting. Mr H. Jaques, who was elected as President, gave his Presidential Address on "The Industry under War Conditions."

### **Annual Conference**

It was decided that the time was inopportune for holding a Conference and the event was therefore cancelled.

### **Publications Committee and the "Journal"**

The war has greatly curtailed the activities of the Regional Sections of the Institute and has thus cut down drastically the amount of material available for reproduction in the Proceedings Section of the "Journal." Written contributions to this Section have appeared during the year and these have contributed materially in a period of dire need.

Again the Transactions Section has been a source of anxiety, few papers having been submitted. When it is considered that the textile industry considered as a whole is second in magnitude only to agriculture, it is a matter for great regret that so few research papers have been submitted by independent workers, and that such a small proportion of the results of research is released for publication.

Although in 1940 the volume of matter in the Abstracts Section was not appreciably different from that in 1939, a marked shortage of material for abstracting was noticed towards the end of the year and the non-availability of certain Continental publications necessitated the reproduction of abstracts from other abstracting journals. It will be appreciated that, in the past, reproduction of abstracts prepared by non-textile organisations has been avoided as far as possible.

Compared with 1939, the total volume of the *Journal* shows a decrease. There were no special numbers corresponding to those of July and September, 1939, containing respectively the papers read at the Annual Conference in Bath and the Textile Section of the British Association in Dundee.

### **The Diplomas Committee and Institute Diplomas**

At the Institute's Examination in Analysis and Testing of Textile Materials held in May, 1940, there were 2 candidates, 1 being successful. This examination opens the way for members in the distribution trade to qualify for the Associateship.

The Institute's Examinations for the Associateship Diploma were held as usual in 1940. The Preliminary Examination was held on 22nd May, 1940, in Manchester, and the Examination in General Textile Technology was held on the 29th May, 1940, at Belfast, Bradford, Dunfermline, Leicester, London, Manchester and Bombay. In the Preliminary Examination there were 5 successful candidates from a total of 8, and 1 candidate was successful in Essay. In the Examination in General Textile Technology, 28 candidates were successful out of a total of 42.

Applications for the Institute Diplomas during 1940 totalled 60 (15 Fellowship and 45 Associateship), as against 85 in the previous year (21 Fellowship and 64 Associateship). The total number of applications since the Charter was granted in 1925 reached 1,222 (361 Fellowship and 861 Associateship).

### **Textile and Designs Committee: Institute Competitions**

In view of the demand that was made for the continuation of the Competitions during the war period, it was decided to hold all sections as usual. The number of entries was very pleasing and gives some indication of the success which is being attained by the Scheme. Again a Prize Distribution was held in each of three areas, and winning albums were exhibited on each occasion. Prizes were distributed by Mr J. Crompton, at Bradford, Mr. H. Haygarth Jackson, at Burnley, and Mr P. A. Bentley, at Leicester and Nottingham.

The total number of entries in 1940 was 134, as compared with 171 in the previous year. Special thanks are recorded to the following firms for gifts of fabrics in connection with the Reference Collection issued this year—Courtaulds Ltd, British Celanese Ltd, Vantona Textiles Ltd, W. M. Miller & Co., Ltd, Whitworth & Mitchell Ltd, Tootal Broadhurst Lee Co., Ltd, Marshall Fabrics Ltd, Driver, Hartley & Co., Ltd, Philip Pariser & Sons, Ltd, John Halliday & Sons, Ltd, Turnbull & Stockdale Ltd, Thos. French & Sons, Ltd, Nottingham Lace Federation and British Colour Council, and Ministry of Supply.

The Prize money for "E" Competition was given by Mr P. A. Bentley, of Leicester.

### **National Certificates in Textiles**

It is gratifying to note that students are still able to proceed with their training even during war time. In 1940, there were 144 (241) candidates for the Ordinary and Higher Certificates, 113 (186) Certificates being awarded, 12 (13) with Distinction; (the figures in brackets are for 1939). Seventy courses are now recognised in 27 Colleges and Schools.

### **Section Activities**

It has still been possible to hold some section meetings and lectures although facilities are naturally restricted by the prevailing conditions. The following meetings were held during the year—

Irish Section, one meeting, Lancashire Section, five meetings, London Section, four meetings, Midlands Section, two meetings, Scottish Section, one meeting, Yorkshire Section, eight meetings.

### **Editorial Board and Library**

The year under review brings the first fruits of the work of the Editorial Board. The first portion of a work on Mechanics by Mr W. A. Hanton appeared in August, and has been favourably reviewed. The Institute is acting as its own publisher and book-seller.

Good progress has been made, and consideration is being given to further books.

The Library Committee decided that the issue of a new catalogue should be postponed during the present emergency. The Library service has been maintained and the number of books and periodicals borrowed by members has been larger than usual. The Committee wishes to place on record its appreciation of the gift of books from the library of Mr H. Nisbet.

### **Frank Wright Memorial Fund**

It will be remembered that in 1939, Mrs Wright promised to give £1,000 to the Institute for the purpose of creating a fund to commemorate the memory of the late Mr Frank Wright, who was a strong supporter of the Institute for many years. With Mrs Wright's approval, arrangements are being made for the income from the Fund to be used for the encouragement of research in the cotton spinning, doubling and twisting industry. It is intended that the fund shall assist research workers in cases where they are unable to cover the whole cost of their investigations themselves.

### Recruitment, Selection and Training of Textile Operatives

A committee has been formed to consider the subject of Recruitment, Selection and Training of Textile Operatives. Committee members, both industrial and teacher, and representing all sections of the textile industry, have supplied valuable information. Although conditions ruling at the present time are abnormal, the Committee hopes to be in a position to make a very useful contribution on this important topic when conditions are more settled. It is felt that now is the time to prepare for future action.

### Service Medal

A new medal was instituted during 1940, to give some practical evidence of the Institute's appreciation of valuable service to the Institute. Mr. Down, who had filled the position of Hon. Secretary to the London Section so well from 1925 to 1940, and Mr. Shannon, who had done work of equal merit in a similar position for the Irish Section between 1926 and 1939, were both awarded this medal. The Honorary Life Membership was conferred on Mr. A. W. Blair, in recognition of his services as Hon. Secretary of the Scottish Section from 1929 to the present time. The Institute sincerely appreciates the very capable and highly valuable work of these members.

### Employment Register

This section of the Institute's activities still continues to be of assistance both to the industry and to Government Departments. A special Register was formed of members who were prepared to use their textile knowledge in work of national importance. From this register it has been possible to make recommendations which have been considered when filling vacancies.

### Standardisation in Textiles

When the Institute undertook this work the plan approved covered an initial period of three years, which came to an end in 1940. A Report was accordingly prepared which, on the authority of the Executive, was published in the January, 1941, number of the *Journal of the Textile Institute*.

Few changes in the original organisation have proved necessary. In the two years during which technical work has been under consideration, the progress, in view of the fact that the scheme is an entirely new development, has been steady and satisfactory. Two British Standards (Textile) have been published by the British Standards Institution and a third is ready for issue. The preparatory work on several others has reached an advanced stage.

### Council and Committee Meetings

The following is a record of meetings held during 1940: Council, 9; Finance and General Purposes, 11; Emergency, 5; Publications, 11; Development, 2; Diplomas, 11; Joint Committee re National Certificates, 4; Textiles and Designs, 5; Scholarships, 2; Unification of Testing Methods, 1; Editorial, 5; Library, 1; Recruitment, Selection and Training of Textile Operatives, 4; Spanish Handbook, 2; Lancashire Section, 3; London Section, 1; Midlands Section, 1; Yorkshire Section, 1. In addition 3 Sub-Committees met for the consideration of special matters.

The total number of meetings for 1940 was 79, as against 81 in the previous year.

### Membership

The membership list at the end of 1940—to be carried forward to 1941—was made up as follows:—Honorary Life Members, 12; Life Members, 44; Ordinary Members, 1,554; Junior Members, 133. Total 1,743, as against 1,757 at the end of 1939. Of the numbers at 31st December last, 203 had been admitted to the Fellowship and 435 to the Associateship.

The Council regrets to announce the loss by death, during 1940, of some prominent members. Amongst these are Colonel F. R. McConnel and Sir William Henderson, both of whom were Foundation Life Members and Fellows of the Institute. In addition Colonel McConnel rendered valuable service to the Institute as President during 1921. Others include J. G. Abel (Aberdeenshire), G. M. Canham (Surrey), T. Halstead (Leeds), S. B. Hollings (Bradford) who was a Fellow, R. H. Kay (Altrincham) who was an Associate, H. W. Lee (Macclesfield), H. W. McClure (Glasgow), I. Miki (London), and R. S. Murr (Selkirk).

### Spanish Handbook on British Industrial Practice

The British Standards Institution have undertaken the production of a Spanish Handbook embodying detailed descriptions of British industrial practice. The Textile Institute have been requested and have agreed to provide the material covering the whole of the Textile Industries. An *ad hoc* Committee has been established under the Chairmanship of Mr. Frank Nasmith, and it has enlisted the services of Associations connected with the development of the various sections of the industry, together with a large body of individual contributors who have intimate and expert knowledge of its several phases. The work is progressing in an extremely satisfactory manner and a number of articles have already been submitted to the British Standards Institution for inclusion in the section.





**Foundation Fund**  
**Income from Investments Account for the Year ended 31st December, 1940**

Cr.

Dr.

EXPENDITURE		INCOME	
1939	1939	1939	1939
£ s d	£ s d	£ s d	£ s d
To Allocation—		By Income from—	
25 0 0 Mather Lecture		£1000 0 0 Leeds Corporation Redeemable Stock less Tax	18 10 0
352 17 6 Revenue Account—General	386 3 4	£569 15 0 3% Local Loans less Tax	9 16 8
37 15 10 Life Membership	37 15 10	£1242 10 0 4% Consols less Tax	29 16 6
182 17 0 Scholarship Scheme	180 5 8	£47 19 6 21% Conversion Stock less Tax	1 3 10
89 7 6 Crompton and Bealand Prize Fund	78 17 6	£1125 0 0 4% L.M.S. Preference Stock less Tax	23 17 6
		£1000 0 0 4% Funding Loan less Tax	23 0 0
		£16939 18 10 3½% War Stock	578 7 10
£687 17 10	£683 2 4		£683 2 4

**Crompton Prize Fund Scheme—Competitions**

**Income and Expenditure Account for the Year ended 31st December, 1940**

Cr.

Dr.

EXPENDITURE		INCOME	
1939	1939	1939	1939
£ s d	£ s d	£ s d	£ s d
To Printing and Stationery	36 9 6	By Albums Subscriptions	147 10 0
" Purchase of Specimens	21 10 11	" Competition Entrance Fees	15 14 0
" Mounting of Specimens	29 10 0	" Donation—P. A. Bentley	12 0 0
" Prize Awards and Expenses	151 11 9	" Dividend on £1000 3½% War Stock	38 0 0
" Postages and Carriage	11 10 10	" Dividend on £1000 3% Leeds Corporation Redeemable Stock	18 0 0
" Administration Expenses	5 0 0	" Dividend on £1125 4% L.M.S. Preference Stock	23 17 6
		" Income Tax Repayment	26 5 0
245 17 10 Total Expenditure for Year	255 13 0		
25 19 2 " Reserve Account—Surplus for Year	4 13 6		
£271 17 0	£260 6 6	Total Income for Year	£280 6 6

**Scholarship Scheme**

EXPENDITURE		INCOME	
1939	1939	1939	1939
£ s d	£ s d	£ s d	£ s d
To Travelling Expenses	0 16 8	By Interest on £4870 3½% War Stock	170 9 0
" Printing and Stationery	— — —	" Interest on £569 15 0 3% Local Loans	9 16 8
5 0 10	— — —		
5 0 10	0 16 8		
177 16 2 " Reserve Account—Surplus for Year	179 9 0		
£182 17 0	£180 5 8		£180 5 8



**Dr. The Textile Institute—Revenue Account for the Year ended 31st December, 1940 Cr.**

EXPENDITURE		INCOME	
1939	1939	1939	1939
£ s d	£ s d	£ s d	£ s d
206 10 10	To Rent and Rates	20277 5 0	By Membership Subscriptions (1940)
	Less to Journal Account and Standardisation Account	67 6 6	" Paid in advance in 1939
		215 1 6	" Arrears paid
76 9 4	" Heating, Lighting and Cleaning	21 0 0	" Special Subscription—The Weavers Company
	Less to Journal Account and Standardisation Account	37 15 10	" Interest on Life Membership Investments
		213 13 6	" Diploma Fees
924 17 6	" Salaries	3482 2 4	Less Amount transferred to Journal Account
	Less to Journal Account and Standardisation Account	909 5 6	
401 14 0	" Wages	2572 16 10	" National Certificates, Competition and Scholarship
	Less to Journal Account and Standardisation Account	115 0 0	" Schemes—Administration Expenses
		352 17	" Foundation Fund—Income from Investments
		- - -	Account
			Income Tax Repayment
91 17 7	" Pension Fund Contributions	314 5 4	
47 5 0	" Savings Association Contributions	91 17 7	
106 1 7	" General Expenses	40 15 0	
120 1 9	" General Printing and Stationery	119 12 3	
108 2 9	" Postages, Telegrams and Telephones	145 14 2	
7 7 2	" Insurances	78 15 6	
174 14 9	" Audit and Legal Charges	10 12 2	
29 1 0	" Subscriptions to Institutions	77 18 10	
- - -	" Income Tax	4 4 0	
101 2 0	" Depreciation on Furniture	273 11 6	
148 - - -	" Painting and Decorating	102 18 8	
186 7 8	" Section Expenses	25 0 0	
58 7 3	" Annual Conference Expenses	131 1 10	
26 19 1	" Meeting and Travelling Expenses	- - -	
103 17 6	" Library Account	42 16 6	
2 11 6	" Editorial Board	29 11 4	
50 0 0	" Diplomas Account Expenses	5 6 1	
4 12 8	" Media Account	124 0 5	
	" Grant to Standardisation Account	21 15 0	
	" Bank Charges, less Interest	50 0 0	
		6 8 7	
2978 9 7		2487 14 0	
62 4 9	Surplus Income over Expenditure for Year 1940	529 14 10	
£3040 14 4		£3017 8 10	
		£3040 14 4	
		£3017 8 10	

**THE TEXTILE INSTITUTE**  
**SCHEDULE OF INVESTMENTS**

(at Cost or Value at Original Date of Gift) as on 31st December, 1940

				FOUNDATION FUND			
<i>General Account—</i>				£	s	d	£ s d
£3737	14	9	3½% War Stock	3503	7	0	
4789	9	5	Do	4789	9	5	
48	16	3	Do	49	14	1	
105	5	3	Do	106	14	0	
102	17	6	Do	105	16	0	
240	0	0	Do	246	10	9	
650	0	0	Do	661	9	6	
194	9	2	Do	200	0	0	
1000	0	0	4% Funding Stock, 1960-90	800	0	0	
1242	10	0	4% Consolidated Stock	1050	0	0	
							11513 0 9
<i>Scholarship Scheme—</i>							
£4870	0	0	3½% War Stock	5002	13	3	
569	15	0	3% Local Loans	500	0	0	
							5502 13 3
<i>Crompton and Beanland Prize Fund—</i>							
£1000	0	0	3½% War Stock	1000	0	0	
1125	0	0	4% L M S Railway Preference Stock	1500	0	0	
1000	0	0	3% Leeds Corporation Redeemable Stock, 1955-58	1015	1	0	
							3515 1 0
<i>Life Membership Account—</i>							
£52	5	0	3½% War Stock	53	14	6	
50	0	0	Do	51	5	6	
99	1	6	Do	97	10	0	
47	19	6	2½% Conversion Loan, 1944-49	50	0	0	
							252 10 0
<i>Frank Wright Memorial Fund —</i>							
£1000	0	0	3½% War Stock				1000 0 0
£21925	3	4	Nominal Value				£21783 5 0

The Market Value of the above securities on  
31st December, 1940, was approximately £22,031 1s 4d  
(Securities are at National Provincial Bank Ltd )

Audited and found correct,  
70 Spring Gardens, Manchester, 2  
6th March, 1941

ARTHUR E. PIGGOTT, SON & CO,  
Incorporated Accountants, Auditors

## PRESIDENT 1941

Mr. G H Thompson, J P, F T I., of Oldham, who was elected President at the Annual General Meeting, has a long record of valuable service both to the Textile Institute and to the textile industry. In addition to being a Justice of the Peace and a Circuit Steward, he is also President of the Federation of Textile Works Managers, and on the Council of both the Chamber of Commerce of the British Empire and the Empire Cotton Growing Corporation. He has spent a lifetime in textiles and has travelled extensively. At the present time he is Manager and Executive Director of a large textile company and is a member of many Government advisory Committees. Mr. Thompson has been a member of the Council since 1932, and since that time has served on many of the Institute's Committees, working conscientiously in every position that he was able to accept. The Institute can count itself fortunate in having the services of Mr. Thompson as President during the ensuing year.

In his Presidential Address, Mr. Thompson said  
Gentlemen,

For a President entering office there is a sort of standard domestic talk. He is expected to give a resumé of the work done. He is expected to tell what the organisation stands for and to outline the policy for the future.

If you are expecting such an oration from me, I am afraid you will be disappointed, for the work accomplished is excellently set out in the Council's Annual Report, and the retiring President has supplemented it in an admirable manner.

It is unnecessary to dwell upon the objects of the Textile Institute since you know them as well as I do. These objects remain unchanged even in critical times like the present. Since world wars cannot be waged without repercussions in nearly every walk of life, it is not surprising that our activities have been affected. Transport difficulties intensified by the black-out have interfered to some extent with the programme of our Regional Sections, but brave efforts are being made to carry on as in happier times.

Some difficulties have been encountered in the production of the *Journal*, but continuity of publication has so far been maintained. There has been some slight diminution in size, but the format and style have not been changed. I do not know what your personal experience of the *Journal* has been, but I used to meet a criticism fairly freely that the *Journal* was too highbrow for the man in the factory. I have for many years been associated with the publication of the *Journal* and know that it has not changed. Yet to-day I hear very little of that criticism that a few years ago was common, and I sometimes wonder if the man in the factory is becoming increasingly conscious of the connection between science and practice.

To give an outline of the future policy of the Institute in these troublous times would be decidedly futile and somewhat dangerous. Prophecy is altogether too risky a business for practical men such as ourselves. Yet we might legitimately ask about our duty as Textile Technologists to the world of to-day. We all know that the industry has need of us and that there is considerable likelihood of this need becoming greater and more urgent. I have no doubt that such grave questions exercise your minds. From this it is not a big step to ask ourselves what are to be our special responsibilities in the world of to-morrow. The answer to this is not so easy, but I think it safe to say that both individually and collectively we shall require vision, imagination and courage. There will arise new problems and all the pertinent facts will require assembling, examining, co-ordinating and analysing. In this there will be much work to do. This is a road along which the Institute hopes to help its members. It is our job to light up this road to the best of our ability.

One of the changes taking place at this time may have very far-reaching effects on many of our members. I refer to the Government changes in the



*[By courtesy of Allied Newspapers Ltd.]*

GEO H THOMPSON, Esq, J P, F T I  
PRESIDENT 1941-42



running of Industry This means very great changes with results difficult to visualise or comprehend I have in mind the Government's intention of concentrating production in fewer factories, working full time For some time the Government has pursued the policy of restricting civilian consumption and numerous problems arise in consequence, not the least of these being, short-time working, diminishing turnover and rising costs A further complication, however, is the change from what we might term the free competitive basis to the entirely new one of compulsory nationalisation which required some measure of readjustment But this new policy of concentration of production in fewer factories is likely to cause many uprootings No doubt such a scheme of working will satisfy the principal essential and immediate requirements, sufficient to meet Government orders It is desirable to maintain the greatest possible export trade in view of the shipping situation

The major textile industries are very much involved, for they are now the chief source of what might be termed factory trained Labour, the type perhaps best fitted for munitions The demand for labour for munitions is extremely heavy and will have to be met Theoretically such a scheme is a short cut to meeting it, but its aftermath may be very serious, and it will require men of goodwill and good faith to grapple with the problems that will arise I may be wrong, I hope that I am, but one can see the danger of inefficiency being excused where it should be condemned

The growth of monopolies may be a serious outcome of such a scheme, and this tendency should be checked The size of a firm is no true indication of its efficiency and there is a danger of the smaller firms being swallowed up Time alone will indicate the wisdom of the steps now being taken, but unless men of goodwill keep these things in mind, we may find that the post-war textile industry has moved in a retrograde direction

This Institute, with the help of the many who wish it well, will endeavour to function to the maximum efficiency, taking into consideration the limiting circumstances imposed by the times If these should prove too formidable, some of the activities may have to be diminished or even laid aside for a time One feels that with the goodwill, the enthusiasm and the fine team spirit that permeates the Council and the various committees, that however great the difficulties, a higher degree of resolution and responsibility will willingly be undertaken to further the work of this Institute

Between the development of science and its applications, especially fundamental science, there is inevitably a time lag This applies to a smaller extent in the case of industrial research, and it would seem that the faculty to use new scientific facts is much rarer than the ability to discover them This perhaps points to a lack of alertness and even courage and enterprise In some cases it is just a question of innate conservatism and natural repugnance to change If by our work we can reduce this time lag, we are doing a good piece of work and our monthly *Journal* is surely playing its part in this direction It ought to be possible to increase the membership of this Institute very greatly, for the textile industry is one of Britain's major activities Let each one of us tell some friend what membership of the Institute means to him, and in doing so we shall not only have done a kindly action, but we shall have made a contribution to progress I appeal to you to keep this in mind Some may think that it is hardly the time to increase our membership In my opinion, however, we should all be stimulated by the many problems which are arising to-day Let us accept them as a challenge and by gathering together those men who are interested in the progress of textiles combat with all our efforts the difficulties with which we are confronted

Gentlemen, there is something more in the power of human will to overcome opposing circumstances than psychologists, philosophers or even ordinary men have fathomed Courage, hope and a genial pugnacity will carry us far along the way to our desired goal.

## IRISH SECTION ANNUAL MEETING

The Annual Meeting of the Irish Section was held at the College of Technology, Belfast, on Tuesday, 25th March, 1941. Professor F Bradbury was in the chair in the absence of Mr. W. H. Webb, through illness

The three vacancies which occurred on the Committee were filled by the following members, who were re-elected.—T Bleakley, H J Dorman, W H Webb

Mr W. H. Webb was recommended for re-election as Chairman during the coming year

An innovation to the effect that four Committee meetings be held during each session in June, September, November and January, was unanimously adopted. It is hoped that by these means the committee will be able to stimulate further activities within the Section

In the report on the past year the Honorary Secretary said that the activities had been affected by war conditions, a large percentage of workers having undertaken some form of voluntary National Service. Two meetings had, however, been held during the winter. At the first one, Mr Webb had given a paper on "The Future of the Linen Industry," and afterwards had presented the Institute's Service Medal to Mr F J W. Shannon, in recognition of his services as Honorary Secretary of the Section for so many years. A second paper, on "Humidity Control and Measurement," had been given by Mr. D S McIlhagger, at a later meeting, when he had illustrated his lecture with lantern slides and apparatus

The total membership of the Section was approximately the same

A series of interesting visits and lectures were recommended for the Committee's consideration for stimulating interest in the summer and winter sessions.

## LANCASHIRE SECTION ANNUAL MEETING

The members of the Lancashire Section met for their Annual Meeting at the Institute, in Manchester, on Saturday, 22nd March, 1941, when Mr W English, the Chairman, presided

The following members were elected to the Committee for a period of three years —

W A. Hanton	F. Ibbetson	J. Starkie
B Hesketh	G Moores	P Webb
W Heywood	F. Scholefield	W Wilkinson

The Chairman gave the report for the past session and stressed the importance of continuing the work of the Institute in spite of present difficulties. He pointed out that the membership of the Section was approximately the same as in the previous year.

Discussion took place on the future programme of the Section. It was suggested that summer meetings might be held and joint lectures arranged with local associations

The business meeting closed with a hearty vote of thanks to the Chairman

Mr H. Rostron then gave a lecture on "Selection and Training of Textile Operatives," which was followed by discussion. A report of the lecture will be given in an early issue of the *Journal*

At a subsequent Committee meeting, Mr B Hesketh, of Farnworth, was unanimously elected Chairman of the Lancashire Section for the new session

## LONDON SECTION ANNUAL MEETING

The Annual Meeting of the London Section was held at the offices of The Rayon and Silk Association, at High Holborn, on Friday, 28th March, 1941. The Chairman of the Section Committee, Mr W. H. Matthews, presided, and read the Annual Report for the past year.

From the report it was seen that the total number of members was slightly lower but the decrease was explained by the transfer of members from the London

area to northern towns. There had been one paper read to the Section during the session, but apart from this, circumstances made it impracticable to arrange further meetings or visits. Mr Matthews said that the Committee had met on a number of occasions and had recently arranged for an enquiry to be addressed to members with regard to the possibility of resuming activities. He reminded members of the presentation of the Institute Service Medal to Mr A R Down, in recognition of his work as Honorary Secretary.

The Committee's Report wished to place on record its appreciation of the services rendered to the Section during the past year by the Chairman, Mr W H Matthews, and the Hon Secretary, Mr H. R. Murray Shaw. It was also desired to thank the Rayon and Silk Association (Inc) for the use of its Board Room.

The following six retiring members were re-elected to serve on the Section Committee for a period of three years —

E W Goodale	F C Harwood	L S Irvine
H. R. Murray Shaw	C Sunderland	J Guilfoyle Williams

It was unanimously agreed to recommend the re-election of Mr W H Matthews as Chairman of the Section for a second year.

After considering the returns from the enquiry addressed to members, it was decided that a luncheon meeting should be held towards the end of April, and that after this meeting had taken place, consideration should be given to the possibility of having other meetings in the near future.

### MIDLANDS SECTION ANNUAL MEETING

Mr W Pritchard, Chairman of the Section Committee, presided at the Annual Meeting of the Midlands Section, held at the Mechanics Institute, Nottingham, on Saturday, 22nd March.

In the Annual Report the Hon Secretary said that there had been an increase in membership of the Section. So far as meetings were concerned, a good start was made at Coventry, when the Coventry Textile Society came into being. This society was to be congratulated on the most successful first season that it had completed. Other meetings of the Section could not be held, however, in view of the prevailing conditions. Reference was made to the activities of various members on the Institute's Committees, and to the support of the Annual Competitions in the Midlands.

The members of the Committee elected to fill the six vacancies were —

W E Boswell	W A. Dutton	F Hern
G H Buckley	J K Ebbelwhite	W Pritchard.

Several suggestions were received for lectures. In addition a new procedure was adopted when it was decided to have localised discussion groups. These were tentatively arranged for Nottingham, Leicester, Loughborough, and Derby.

The meeting closed with hearty votes of thanks to the Chairman, to the Hon Secretary, and to Mr Stoppard, for his excellent arrangements for the meeting.

The Committee meeting which followed was unanimous in re-electing Mr W. Pritchard as Chairman for the ensuing year.

### SCOTTISH SECTION ANNUAL MEETING

The Scottish Section held its Annual Meeting at the North British Station Hotel, Edinburgh, on Saturday, 17th March, 1941.

Mr. W H Wilkinson, the Chairman, gave a short report of the previous year. He said that because of the fact that members of the Scottish Section were so scattered and in view of war conditions, it had not been considered advisable to hold any lectures or visits. It was hoped, however, that some functions would be possible in the future. The membership of the section was approximately the same.



There were three vacancies on the Committee and these were filled by —  
 A R Geary                      A P. Mieras                      W. Watson

The Meeting wished to place on record its appreciation of the work carried out by Mr Blair, as Hon Secretary, and for which he had been awarded Honorary Life Membership of the Institute

After the business meeting a discussion took place on the recognition by the industry and by government departments of the Institute's diplomas. The fact was deplored that as a result of changes in the reservations, the industry might suffer a serious loss of qualified textile technologists.

The meeting closed with a vote of thanks to the Chairman

### YORKSHIRE SECTION

Mr. H. Hardy, Chairman of the Section Committee, presided at the Annual Meeting of the Yorkshire Section, held at the Midland Hotel, Bradford, on Thursday, 27th March, 1941.

The Hon Secretary, giving the report for the previous session, said that lectures held had been a surprising success, despite the disturbances caused by the war. The average attendance for the six meetings had been 35. He reminded the members of the presentation made in recognition of the valuable work that Mr Garner had done as Hon Secretary. Other members of the committee had given very useful assistance in compiling the wool section of the Spanish Handbook on British Industrial Practice. The total membership of the Section was slightly increased and showed a satisfactory state of affairs. The report was unanimously adopted.

A resolution that diplomas should be presented to Fellows and Associates at Section Meetings was adopted.

It was reported that eight nominations had been received for the eight vacancies on the Committee, and the following members were declared elected for a period of three years —

S N Blagbrough	C. M Kershaw	J B Speakman
H Haigh	W E King	D Wilson
H Hardy	S. Shann	

A discussion took place on the reports of Section Meetings in the Institute's *Journal*, and several recommendations were made in this connection.

During the meeting, votes of thanks were expressed to Mr. H. Hardy, Mr W. Garner, Mr R E Masters, and Mr C M Kershaw, for their work in the Section.

At the Committee meeting which followed, Mr W Garner was elected as the new Chairman, and Professor J B Speakman was elected Vice-Chairman. Mr R. E Masters and Mr C M Kershaw were re-elected as Hon. Secretary and Hon. Assistant Secretary respectively.

## Institute Membership

Elections to Fellowship and Associateship has been completed as follows, since the appearance of the previous list (February issue of the *Journal*) —

### FELLOWSHIPS

NORMAN CECIL GEE, Esq, A T I,

Head of Textile Department, Municipal Technical College, Dewsbury

RONALD WILLIAMSON, Esq, A T I,

Assistant Manager, Messrs York Street Flax Spinning Co, Ltd, Belfast

CARL C MATTMAN, Esq, Junr,

Fabric Technician and Manager of the Fabric Development Dept, A M Tenney Assoc., Inc, New York.

### ASSOCIATESHIPS

CECIL LESLIE HARRIS                      THOMAS ERIC ELLISON

LEONARD SMETHURST                      LUCAS ALEXANDER REX WARING.

FREDERICK JOHN ALEXANDER

### New Members

The following applicants were elected to membership at the April meeting of Council —

- J W B Ashby, Courtaulds Ltd, Greenfield, Holywell, N Wales (Technical Manager)  
 F Bramma, 22, Glenaire Drive, Baildon, Shipley, Yorks (Weaving Instructor)  
 W Brown, c/o The Watford Steam Laundry Ltd, Sydney Road, Watford, Herts (Laundry Manager)  
 W M Murdoch, Harwood Cash & Co, Ltd, Lawn Mills, Mansfield (Director)  
 C Sackfield, 108, Moss Lane, Swinton, Nr Manchester (Head Carder, John Ashworth (1902) Ltd, Pendlebury)

### Employment Register

The following announcements are taken from entries in our Register of Members whose services are on offer. Employers may obtain full particulars on application. —

- No 223—Young man, 31 years of age, desires position as Manager in Worsted Spinning 16 years' experience of mill routine in cone and open drawing, fly and cap spinning 3 years' experience as College instructor City & Guilds Full Technological Certificate Prepared to take post in British Empire or U S A
- No 224—A T I 33 years of age, desires position as Weaving Manager in England 10 years' experience with various types of Automatic looms and Preparing Machinery 5 years' Research and Testing (Mill) Cotton, Linen, Rayon fabrics 3 years' Weaving Manager abroad Evening lecturer in Weaving Knowledge of languages
- No 225—Young man, 29 years of age, A T I desires position as Dye-House Chemist, Manager or Under-Manager Seven and a half years' experience as Assistant Dye-House Chemist and 2 years as Dye-House Chemist City & Guilds of London Institute Full Technological Certificate for Silk and Rayon Dyeing.

## NOTICES: INSTITUTE MEETINGS

- Tuesday, 3rd June—*Manchester*—1 30 p m Meeting of the Publications Committee at the Institute
- Wednesday, 11th June *Manchester*—2 30 p m Meeting of the Finance and General Purposes Committee at the Institute
- Wednesday, 11th June *Manchester*—2 45 p m Meeting of the Diplomas Committee at the Institute
- Wednesday, 18th June *Manchester*—11 30 a m Council Meeting at the Midland Hotel
- Wednesday, 18th June *Manchester*—Luncheon and Mather Lecture at the Midland Hotel

### LANCASHIRE SECTION

- Tuesday, 24th June *Manchester*—6 0 p m Lecture "Textile Finishing in War-time" by R J Smith, Esq, at the Institute premises

### OTHER ORGANISATIONS

*Textile Teachers*—Lancashire Section

- Saturday, 14th June *Manchester*—Annual Meeting at the Textile Institute, 16, St Mary's Parsonage, Manchester.

## General Items

### **Mather Lecture**

The Mather Lecture will be given at the Midland Hotel, Manchester, on Wednesday, 18th June, 1941, by Professor J B Speakman, D Sc, F I C, F T I, Professor of Textile Industries at Leeds University. The subject will be "The Chemistry of Wool and Related Fibres", and the lecture will form part of the programme of the Luncheon and Meeting which is being held in place of the Annual Conference.

### **Technical Editor**

Mr W J Hall, B Sc, who has held the position of Technical Editor at the Institute for a number of years, has now been granted leave of absence in order to take up a position with the Ministry of Supply. The appointment has arisen through the Central Register. The Council and all members of the Institute will extend their good wishes to Mr Hall in the war work which he has undertaken.

On the invitation of the Publications Committee, Professor W E Morton, of Manchester College of Technology, has agreed to deal with the Proceedings Section of the *Journal* during the absence of the Technical Editor. The Committee wishes to record its appreciation of Professor Morton's assistance.

### **Library**

The Council of the Institute has decided to move part of the Institute's Library into a safer place. One of the members has kindly agreed to take charge of the books during the war period and it will still be possible for members to borrow books as before. There may, however, be some little delay in dealing with requests. Application to borrow books should be made as usual to the Librarian, The Textile Institute, 16, St. Mary's Parsonage, Manchester, 3.

# THE TEXTILE INSTITUTE

*Head Offices*—16 St. Mary's Parsonage, Manchester 3

*Office Hours* 9 a.m. to 5.30 p.m. Weekdays      9 a.m. to 12 noon Saturdays

*Telephone* BLACKFRIARS 2016, MANCHESTER

## OFFICERS OF THE INSTITUTE AND PERSONNEL OF COMMITTEES FOR 1941-42.

At the meeting of Council on 21st May, 1941, the Honorary Officers and personnel of Committees for the year 1941-42 were elected. The following is a complete list of Officers, members of Council and personnel of Committees

### OFFICERS AND COUNCIL

*President* G. H. THOMPSON, J.P., F.T.I.

#### *Past Presidents*

LORD ROTHERHAM 1910-12*	Lieut.-Col. B. PALIN DOBSON 1929-31*
SIR WILLIAM PRIESTLEY 1913-14*	GEO. GARNETT J.P. F.T.I. 1931-33
SIR WILLIAM MATHER 1915-17*	SIR W. CLARE-LEES O.B.E. J.P. 1933-34
SIR FRANK WARNER 1918-19*	SIR THOMAS ROBINSON K.B.E. J.P. 1934-35
SIR HERBERT DIXON 1920*	WILFRED TURNER J.P. F.T.I. 1935-37
Col. F. R. McCONNEL, F.T.I. 1921*	JOHN CROMPTON O.B.E. F.T.I. 1937-38*
JOHN EMSLEY J.P. F.T.I. 1922-26	FRANK NASMITH F.T.I. 1938-39
WM. HOWARTH J.P. 1926-29*	ERNEST W. GOODALE M.C., 1939-40
H. JAGUES, A.S.A.A., 1940-41	

\* Deceased

#### *Vice-Presidents*

F. W. BARWICK	J. H. LESTER	W. R. WADSWORTH
J. H. BATES	W. W. L. LISHMAN	W. H. WEBB
W. KERSHAW	T. C. PETRIE	E. WILDT

*Chairman of Council* W. KERSHAW

*Vice-Chairman of Council* G. HAIGH

*Honorary Secretary* F. NASMITH

*Honorary Treasurer* W. W. L. LISHMAN

#### *Ordinary Members of Council*

H. C. BARNES (Manchester)	W. E. KING (Bradford)
H. BROMILEY (Bolton)	R. LORD (Manchester)
F. CHADWICK (Preston)	W. E. MORTON (Manchester)
W. B. CROMPTON (Bispham)	H. NISBET (Manchester)
J. E. DALTON (Leeds)	F. PICKLES (Leeds)
W. DAVIS (Nottingham)	W. PRITCHARD (Derby)
J. DAY (Dewsbury)	J. READ (Worsley)
N. C. GEE (Dewsbury)	H. RICHARDSON (Bradford)
H. GREENWOOD (Bury)	F. P. SLATER (Bollington)
H. G. GREG (Styal)	J. B. SPEAKMAN (Leeds)
G. HAIGH (Bradford)	A. W. STEVENSON (Galashiels)
F. COURTNEY HARWOOD (London)	A. J. TURNER (Co. Antrim)
WM. HOWARTH (Bolton)	H. A. TURTON (Nuneaton)
F. KENDALL (Bradford)	W. WILKINSON (Blackburn)
S. KERSHAW (Halifax)	J. C. WITHERS (Manchester)

## STANDING COMMITTEES

The following are *ex-officio* members of all Committees (except Diplomas Committee)—  
the President, the Chairman of Council, the Hon. Treasurer, and the Hon. Secretary

### EMERGENCY COMMITTEE

Chairman F NASMITH

H C BARNES	W W L LISHMAN	F NASMITH	J C WITHERS
W KERSHAW	W E MORTON	G H THOMPSON	

### FINANCE AND GENERAL PURPOSES COMMITTEE

Chairman II JAQUES

G HAIGH	H JAQUES	F NASMITH	W PRITCHARD
W HOWARTH	W W L LISHMAN	F C PORTER	J READ
J H LESTER			

together with Chairmen of Publications Committee, Council, Unification of Testing Methods Committee, Vice Chairman of Council, and Immediate Past Chairman of Council

### DIPLOMAS COMMITTEE

Chairman J E DALTON

F W BARWICK	F C HARWOOD	F C PORTER	A W STEVENSON
H BROMLEY	F L GOODALL	H SALT	A J TURNER
J E DALTON	W E KING	F SCHOLEFIELD	E WILDT
W DAVIS	J H LESTER	J B SPEAKMAN	W WILKINSON
*J R S GOODALL	W E MORTON	A K N SPENCER	J C WITHERS

### PUBLICATIONS COMMITTEE

Chairman G H THOMPSON

F W BARWICK	R P FOULDS	W E MORTON	J B SPEAKMAN
A W BAYES	F L GOODALL	H NISBET	A W STEVENSON
P W CUNLIFFE,	W KERSHAW	J W PENNINGTON	G H THOMPSON
W DAVIS	W E KING	J READ	C M WHITTAKER
J DUMVILLE	J H LESTER	F P SLATER	F C WOOD

and two representatives of the Wool Industries Research Association, two representatives of the British Cotton Industry Research Association, one representative of the Linen Industry Research Association, and one representative of the British Launderers' Research Association

### EDITORIAL BOARD

Chairman II RICHARDSON

A W BAYES	Col W FRENCH	H P PARSONS	I H ROBINSON
P F BURNS	S KERSHAW	F PICKLES	E SWAN
J E DALTON	R McCALL	I READ	C J. WHITELEGG
		H RICHARDSON	

Advisers to the Board: Dr CUTHILL, W A HANTON, J A MATTHEW, F. SCHOLEFIELD, and J B SPEAKMAN

### LIBRARY COMMITTEE

Chairman J READ

H C BARNES	H G GREG	W KERSHAW	W H SLATER
N C GEE	W HOWARTH	II NISBET	B SLATTERY
H GREENWOOD	S KERSHAW	J READ	J C WITHERS
			F C WOOD

### UNIFICATION OF TESTING METHODS COMMITTEE

Chairman W KERSHAW

J ASHWORTH	A W BAYES	B M JONES	F P SLATER
N G BAGULEY	F L GOODALL	W KERSHAW	A J TURNER
J BARR	W H GIBSON	J H LESTER	B H WILSDON
F W BARWICK	F C HARWOOD	J LOMAX	W PRITCHARD

Sir ROBERT PICKARD (Observer)

and two representatives of the Society of Dyers and Colourists

### SCHOLARSHIPS COMMITTEE

Chairman G H THOMPSON

J W BARON	G CLAPPERTON	W HOWARTH	F C PORTER
W T BOOTHMAN	J E DALTON	R LORD	G H THOMPSON
F CHADWICK	H G GREG	F NASMITH	

and two representatives of the Cotton Reconstruction Board

### TEXTILES AND DESIGNS COMMITTEE

Chairman

H C BARNES	W B CROMPTON	J HOLLAS	F C PORTER
J L BESWICK	J GREENWOOD	W KERSHAW	E M ROBERTS
C BOWNAS	H G GREG	R LORD	E WILDT
H BROOKES	G HAIGH	H NISBET	

### INSTITUTE DEVELOPMENT COMMITTEE

Chairman W HOWARTH

H C BARNES	H G GREG	F KENDALL	F NASMITH
J E DALTON	W HOWARTH	W E MORTON	*C G WINSON

Chairmen of Textiles and Designs Committee, Finance and General Purposes Committee and Diplomas Committee

### RECRUITMENT, SELECTION AND TRAINING FOR THE TEXTILE INDUSTRY

Chairman J E DALTON

F W BARWICK	A DRAFER	J READ	G H THOMPSON
H BROMLEY	H G GREG	H RICHARDSON	N TUNSTALL
P F BURNS	A R KELSEY	F J W SHANNON	S E WARD
S A G CALDWELL	S KERSHAW	H A TURTON	W WILKINSON
F CHADWICK	W KERSHAW	A SHAW	
J CHAMBERLAIN	W LOCKHART	J D SPENCER	
J E DALTON	F NASMITH	A W STEVENSON	

\*In H M Forces

# JOINT COMMITTEE re NATIONAL CERTIFICATES

Chairman F W BARWICK

F W BARWICK J E DALTON J H LESTER T H ROBINSON  
and four representatives of the Board of Education

## PROFESSIONAL STATUS COMMITTEE

Chairman

F W BARWICK J H LESTER F P SLATER J C WITHERS  
W KERSHAW F NASMITH

All except the Emergency Committee are Standing Committees

## INSTITUTE SECTION COMMITTEES

### IRISH SECTION COMMITTEE

Chairman W H WEBB

Hon Sec H J DORMAN, College of Technology, Belfast  
To retire in 1942 To retire in 1943 To retire in 1944  
F BRADBURY W J COWDEN W H WEBB  
F J W SHANNON J ASHWORTH T BLEALEY  
A J TURNER N JACKSON H J DORMAN

### LANCASHIRE SECTION COMMITTEE

To retire in 1942 To retire in 1943 To retire in 1944

Chairman B HESKETH

Hon Sec H. P. CURTIS, 44, Brazennose Street, Manchester  
H C BARNES A W BAYES W A HANTON  
F CHADWICK H BROMLEY B HESKETH  
H P CURTIS T L ELLIOTT F IBBETSON  
A DRAPER W ENGLISH W HEYWOOD  
H G GREG W HOWARTH G MOORES  
T E MITCHELL R J SMITH F SCHOLEFIELD  
H NISBET F A J TAYLOR J STARKIE  
F I SHARP S TAYLOR P H WEBB  
G H THOMPSON F C WOOD W WILKINSON

### LONDON SECTION COMMITTEE

To retire in 1942 To retire in 1943 To retire in 1944

Chairman W H MATTHEWS

Hon Sec H R M SHAW, 229-231, High Holborn, London, WC1  
S H CARTER C H COLTON E W GOODALE  
A R DOWN A MASON F C HARWOOD  
A E GARRETT F C PRICE L S IRVINE  
A GOWIE G A RUSHTON H R MURRAY SHAW  
F J HENLEY W H MATTHEWS C F SUNDERLAND  
R S MEREDITH T C PETRIE J G WILLIAMS

### MIDLANDS SECTION COMMITTEE

To retire in 1942 To retire in 1943 To retire in 1944

Chairman W PRITCHARD

Hon Sec T A PORT, 1 Horsefair Street, Leicester  
G DAVIS P A BENTLEY W E BOSWELL  
W A EDWARDS W N BIGNALL G H BUCKLEY  
A S GREENWOOD J CHAMBERLAIN W A DUTTON  
E WILDT W PENN J K EBBLEWHITE  
\*C G WINSON A STOPPARD F HERY  
T A PURT W PRITCHARD

It was recommended to the Midlands Section Committee that Mr H A TILTON should be co-opted as a member of the Committee

### SCOTTISH SECTION COMMITTEE

To retire in 1942 To retire in 1943 To retire in 1944

Chairman W H WILKINSON

Hon Sec A W BLAIR, 29, Montrose Street, Glasgow, C1  
A W BLAIR J C CAMPBELL A R GARY  
A W STEVENSON W LOCKHART A P MIERAS  
R G HARRISON W H WILKINSON W WATSON

### YORKSHIRE SECTION COMMITTEE

To retire in 1942 To retire in 1943 To retire in 1944

Chairman W GARNER

Hon Sec R E MASTERS, Petherton House, Huddersfield Road, Brighouse  
J DUNVILLE A BAILEY S N BLAGBROUGH  
H D HALLIDAY J R EMMS H HAIGH  
J R HIND W GARNER H HARDY  
W MORLEY G HAIGH C M KERSHAW  
H RICHARDSON J R HEALEY W E KING  
T H ROBINSON F KENDALL S SHANN  
G SHACKLETON S KERSHAW J B SPEARMAN  
B R D SHARP F PICKLES D WILSON

\* In H M Forces

# THE JOURNAL OF THE TEXTILE INSTITUTE

Vol. XXXII

JUNE 1941

No 6

## PROCEEDINGS

### NOTES AND ANNOUNCEMENTS

#### INSTITUTE MEETINGS

- Tuesday 1st July *Manchester*—1 30 p m Meeting of the Diplomas Committee at the Institute
- Tuesday 1st July *Manchester*—2.45 p m Meeting of the Publications Committee at the Institute
- Wednesday 2nd July *Manchester*—2 0 p m Meeting of "F" Competition Sub-Committee at the Institute
- Wednesday 16th July *Manchester*—1 45 p m Meeting of the Finance and General Purposes Committee at the Institute
- Wednesday 16th July *Manchester*—3 0 p m Meeting of the Council at the Institute
- Wednesday 23rd July *Manchester*—Meeting of the Joint Committee re National Certificates in Textiles at the Institute.

#### TEXTILE INSTITUTE DIPLOMAS

Elections to Fellowship and Associateship have been completed as follows since the appearance of the previous list (May issue of the *Journal*) —

#### FELLOWSHIP

LEONARD THOMPSON, M Sc Tech,  
Chief Chemist, Highams Ltd, Accrington

#### ASSOCIATESHIPS

MALAY KUMAR MUKHOPADHYAY  
ARTHUR BRAMLEY

#### New Members

The following applicants were elected to membership at the May and June meetings of Council —

C P Atkinson, 23, Lucy Hall Drive, Baildon (Courtaulds Ltd, Bradford)

H R Baines, Burwains, 44, Old Clough Lane, Walkden, Manchester (Technical Assistant, Ministry of Supply)

C F Cape, 1, Villers Street, Gibbet Street, Halifax

A. Davenport, British Enka Ltd, Aintree, Liverpool 9 (General Manager)

G Leather, 231, Green Lane, Bolton (Technical Representative, John Whiteley and Sons, Ltd, Brunswick Mills, Halifax)

A E Ollerenshaw, Moorfield Mills, Halifax (Woollen and Worsted Dress Goods Manufacturer)

J A. Wither, 7, Hesketh Road, Southport (Assistant Director—Cotton Textiles —Ministry of Supply)

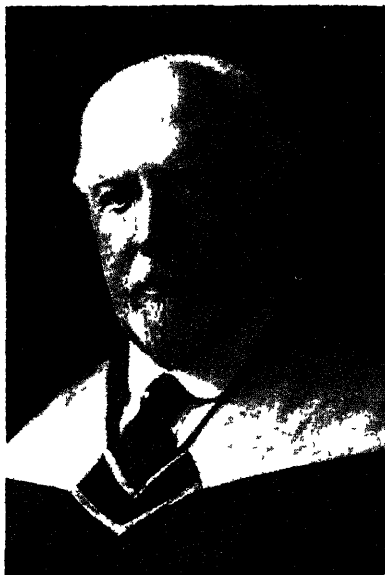
**Employment Register**

The following announcements are taken from entries in our Register of Members whose services are on offer. Employers may obtain full particulars on application.—

- No 224—A T I, 33 years of age, desires position as Weaving Manager in England 10 years' experience with various type of Automatic Looms and Preparing Machinery 5 years Research and Testing (Mill) Cotton, Linen, Rayon fabrics 3 years Weaving Manager abroad Evening lecturer in Weaving Knowledge of languages.
- No 225—Young man, 29 years of age, A T I, desires position as Dye-house Chemist, Manager or Under-Manager Seven and a half years' experience as Assistant Dye-house Chemist and 2 years as Dye-house Chemist City & Guilds of London Institute Full Technological Certificate for Silk and Rayon Dyeing.
- No 226—A T I, 36 years of age 8 years' experience as Assistant Production Manager of Plant producing Rayon Staple Fibre City & Guilds Full Technological Certificate in Cotton Spinning Would prefer to go abroad

**Obituary**

**JOHN CROMPTON, O.B.E., M.Sc.Tech., F.T.I.**



Throughout all his long working life—extending over 50 years—John Crompton worked with a single-minded purpose to improve the knowledge of textile technology. Although very closely engaged in industrial pursuits which busily engaged him, he still found time to pursue persistently his object.

Even as a young man—a youth, in fact—in his pursuit of knowledge he evolved a model loom on which he studied pattern weaving and conveyed his findings to others. Textiles were undoubtedly in his blood.

He was of the family that numbered one of the fathers of the Cotton Industry, namely, Samuel Crompton, the inventor of the Cotton Spinning Mule. His father was a hand-loom weaver of silk fabrics who eventually found his way into a cotton mill in Walkden, where his son joined him at a later date. It was from his father that John Crompton had his first lessons in cloth structure—a



subject in which he so thoroughly perfected his knowledge at a later date by the method previously referred to. His studentship meant long and arduous study, but anyone who was acquainted with John Crompton must have recognised his tenacity of purpose and keen application which could—and did—overcome many difficulties.

He was one of the pioneers of technical education, first as a student and then as a teacher. Subsequently he became an examiner for the City and Guilds of London Institute.

He also contributed articles of value to the technical trade press at a time when textile literature was very scant indeed. In fact, at the end of the last and commencement of the present century there was a spate of articles of varying degree of practical usefulness, but there was a very honest endeavour to fill a big void. Crompton was contemporary with many other well-known writers, such as Beaumont, Fox, Nasmith, Scott Taggart, Thornley, and others like Knecht, and Gardner.

No doubt it was his appreciation of the lack of reliable information that caused him to welcome the advent of the Textile Institute and he was early prominent in the work of that body. Wholeheartedly did he undertake the many demands made upon him, as will be appreciated from the following list of offices he held —

Member of Council, 1918-28

Chairman of Council, 1922-28

Vice-President of the Institute, 1926-37

President of the Institute, 1937-38

Textiles and Designs Committee, 1919-41 (Chairman).

Member of Scholarships Committee, 1930-41

„ „ Development Committee, 1937-41.

„ „ Diplomas Committee, 1924-40

„ „ Finance and General Purposes Committee, 1923-29

„ „ Lancashire Section Committee, 1918-31

„ „ Professional Status Committee, 1926-30

„ „ Propaganda Committee, 1925-30.

„ „ Recruitment, Selection and Training for the Textile Industry, 1940-41.

On the 7th May, 1930, he was awarded the Textile Institute Medal.

He established, in memory of his son, Lieut. Harry Dent Crompton, R.F.C., who was killed in the last War, the Crompton Prize Fund for Textile Design.

For his unstinted labours for the advancement of Textile Technology, the Manchester University conferred on him the degree of M.Sc. in 1923.

As a man he was universally loved. His wise judgment, his patience and his unfailing good temper helped forward the work of the Institute Committees on which he served. His loss as a man is mourned by all who knew him. He has left a vacancy in the ranks of the Institute almost impossible to fill.

### **James F. Copley**

By the death of James F. Copley at the age of 67, in a Salford Nursing Home, on May 1st, the Textile Institute has lost an active member who was a familiar and welcome figure at its Conferences.

He was born in Huddersfield and was educated at the Mechanics' Institute, which was subsequently merged into the Huddersfield Technical College.

He started his business career at the Turnbridge Works, Huddersfield, of Read, Holliday & Sons Ltd. He was in the Aniline Oil Department, which was then under the charge of Dr. Petraczek, who was a man of striking personal appearance and was known inside the Works as the German Emperor. He was a Chemical Engineer who had, no doubt, influenced the bent towards engineering activities which Mr. Copley showed.

He remained with Read, Holliday & Sons for seven years, and subsequently spent a short time in a dyeworks. He devoted himself to the design and manu-

facture of a skein mercerising machine, which activity led him finally to found the firm of Copley, Marshall & Co Ltd, at Wildspur Mills, Newmill, of which he became Managing Director in 1904, and which position he held until his death. His firm's activities included skein and warp mercerising and dyeing, winding and doubling

Fred Copley possessed a very active and versatile mentality and maintained throughout life a keen interest in all educational facilities. In addition to his membership of the Textile Institute he was an active member of the Society of Dyers & Colourists, past President of the Huddersfield Textile Society and a Vice-President of the Huddersfield Engineering Society. He had been a member of the Newmill Rural District Council and was an active Rotarian.

He was a man of many hobbies, one of which was photography, and he was usually very active at our Conferences with a Cine camera. The writer remembers him particularly in this connection during a steamer trip down the Rhine at the Cologne Conference. He had also travelled widely.

He was married in 1899, and is survived by his wife and two daughters, the latter of whom both graduated in science, and at one time were active in their father's business. The writer had known him over a long stretch of years during which we had many friendly technical disputations.

He has left behind him the memory of a friend, who, despite indifferent health, was always cheerful and genial, coupled with an unflagging interest in the latest developments in dyeing and chemistry. The best proof of this is that on entering the Nursing Home in which he died he took with him, as reading matter, two books on chemistry.

#### **Edwin H. Marble**

News has just reached this country that an old member and Fellow of the Textile Institute has passed away in the person of Mr Edwin H. Marble, of Worcester, Massachusetts, U.S.A. Mr Marble had reached the ripe old age of 87 years. He was a president of the firm of Curtis & Marble, Machine Makers, of Worcester, Massachusetts, and he was connected with quite a considerable number of Technical and Scientific Societies. He was a member of the Committee D 13, and was very active in the work of this particular Committee.

## **General Items**

### **Propaganda and Films for the Textile Industry**

The Committee on Recruitment, Selection and Training for the Textile Industry has recently appointed a Literature Sub-Committee. The Sub-Committee is surveying the field of propaganda, in the form of literature and films for the textile industry, which has been prepared either by individual firms or by other bodies. It is felt that members may be able to assist in this work, and if anyone knows of such literature or films the Sub-Committee would be pleased to have details. Communications or copies of books and pamphlets should be addressed to the Acting Secretary, The Textile Institute, 16 St Mary's Parsonage, Manchester, 3.

### **The Industrial Radiology Group of the Institute of Physics**

The formation of an Industrial Radiology Group under the auspices of the Institute of Physics is announced. Its object is to provide a medium for the exchange of information on the practice of radiography and X-ray crystallographic analysis in industry. A committee has been appointed, representing those employing X-rays in industry and the manufacturers of industrial X-ray apparatus and films. Membership of the Group will be open to all interested, whether at present members of the Institute of Physics or not. Fuller details will be published as soon as the Constitution has been formulated. Those interested may register their names with the Honorary Secretary of the Group, Dr L. Mullins, A Inst P, of the Research Laboratories, Kodak Ltd, Harrow, Middlesex, who will send further information as soon as possible.

## London Section

### LUNCHEON MEETING 1st MAY, 1941

#### "The Effect of the War on Textiles"

The Chairman, Mr. W H Matthews, dealt very briefly with the effect of the war on the activities of the London Section. Pressure on members' time, the black-out and other factors, had prevented the execution of a normal winter session programme, and the suggestion for a luncheon hour meeting had arisen at the Annual Meeting of the Section. He was pleased to see such a good attendance and he hoped the discussion to be initiated by Mr Goodale would be such as to convince everyone of the success of this new departure.

Mr E W Goodale, in introducing the subject, observed that it was unnecessary to point out that the effect of the War on textiles could be considered from many points of view. For instance, one could revile the Government, but it was preferable to be not only objective but constructive. There were inevitable restrictions of all kinds but these made the conduct of business very difficult. The raw material controls were set up immediately on the outbreak of war. Amongst other results these had proved effective in keeping down prices. The Wool Control was a specially efficient organisation. The Controls were rendered necessary by the shipping and currency problems.

The rayon industry, it was noted, was at present affected to a smaller extent than the silk, cotton, wool and linen industries. But supplies of certain chemicals essential to the rayon industry were becoming short. The rayon manufacturers exhibited considerable foresight and held substantial stocks of raw materials and chemicals when war broke out.

The effects of the numerous Limitation of Supplies orders issued by the Board of Trade were now being felt in the shops. The operation of some of these orders was being progressively tightened up, e.g., until the last order useful business was done in fabrics containing rayon staple fibre spun on the worsted system.

The Purchase Tax had apparently not had any reducing effect on the volume of business judged by the amount collected during the first two months by H M Customs and Excise. It had, however, adversely affected exports to the U.S.A. and legislation in that country was awaited before the situation could be clarified.

The operation of the Dyestuffs Control has proved benevolent. It has been impartial and has caused no undue hardship. The prohibition of the use of some heavy shades was wise and has resulted in real economy. The work of this Control has been aided by the British Colour Council.

It has been urged that the policy of the Export Licence Department has hampered trade. As regards the new order licensing the export of cotton goods, little can or should be said whilst the matter is at present *sub judice*. The Department's work is intimately associated with the Bank of England in the control of currency problems.

Some held that the continued existence of industry was surprising in view of the many difficulties which could not be avoided and the formalities inseparable from the operation of controls and restrictive orders.

The Chairman thanked Mr Goodale for his rapid yet comprehensive survey. He asked that any remarks he might make during the meeting should not be taken as representative of or committing the Government Department in which he was employed. The principal aims of the Import Licensing Department were the saving of shipping space and economy in foreign exchange and currency.

Captain Brady agreed that the controls were established at the right time and that a useful lesson had been learned in the Great War. The Controls had certainly kept prices down to reasonable levels.

Restrictions and rationing he regarded as absolutely necessary to the winning of the war. Unless there were restrictions the needs of the fighting and other services could not be adequately met and there would also be no export trade. In order to maintain and increase efficiency the concentration of certain industries in fewer establishments was necessary and this was the only way to release skilled labour for munition work. Without controls and restrictions, money would be frittered away as in the Great War, and the post-war problems would be as great as in the 1920 period. The one object of the department in which he served was to win the war and win it as quickly as possible. The shortage of raw materials and the call on shipping for export were most important restrictive factors.

*Mr H. R. Murray Shaw* thought two principal grievances were the long time taken by Government Departments to reach decisions and the insistence on great secrecy when no good purpose was thereby served.

*Captain Brady*, in reply, said that although it was frequently inexpedient to broadcast information, there was no withholding from those entitled to know the facts. The Board of Trade was always willing, for instance, to meet the Chairmen of Export Groups and give information.

*Mr E. W. Goodale* agreed that Chairmen of Export Groups could get information but frequently were not allowed to pass it on to their members. Generally, tactful handling of the Committees overcame the trouble. He admitted that in some cases confidential information was not treated as such and this may have been the cause of the "high policy" of some departments.

*Captain Brady* claimed that the time to deal with questions was not unduly long and many departments were understaffed. Reference to other departments naturally took time but matters of real urgency could be and were decided very quickly.

*Mr A. F. du Plessis* thought there was no need for him to make special reference to wool as *Mr Goodale* had covered it adequately in his general review. He considered the immediate functioning of the Wool Control when war broke out to be a great achievement and a full justification of the shadow control in the period immediately prior to the war. Though a certain amount of hush-hush policy was necessary it should be kept down to the minimum since it so often led to misunderstanding.

He suggested that the future of the raw material controls and the post-war development and control of the textile industries could well be discussed at meetings organised by the Textile Institute.

*Captain Brady* welcomed this suggestion and expressed the view that the operation of the Controls might be a good subject for a Mather Lecture after the War. The meeting approved the sending of this suggestion to the Institute for consideration.

*Mr E. W. Goodale* referred to the use of Trade levies for propaganda purposes. He thought that levies should be compulsory in order to avoid conditions under which non-contributors could benefit from schemes of which they had not borne their share of the cost.

Reverting to the question of confidential information, he said his experience as Chairman of an Export Group showed that, properly handled, the Committee would accept the situation.

He suggested that Controllers of raw materials should have greater executive power. Their actions had too frequently to be referred to the Raw Materials Directorate of the Ministry of Supply.

*Mr A. Mason* said he had hoped that the discussion would turn on substitutes for imported raw materials.

*Mr F C Harwood* said that one result of control was to stimulate substitutes. He asked who was responsible for the composition of blends, and in particular the introduction of 4 per cent wool in fabrics for underwear for the services.

*Mr A F du Plessis* expressed the hope that no substitute for wool would be used in fabrics for export to the U.S.A. The replacement of wool by artificial fibres entailed large economic problems. Normally the saving effected by substitution was small but the subject was very controversial.

*The Chairman* defended Civil Servants dealing with technical problems. They do refer to expert technologists rather than give arbitrary decisions.

*Mr E W Goodale* remarked that Service Departments are now more sympathetic than in the past regarding amendments to specifications proposed by the representatives of industry.

*Mr H R Murray Shaw* referred to the need for a general survey and revision of Service Specifications.

*Mr F C Harwood* said that there was an increasing tendency to consult the industry. The Directors of Research Associations were called to Conferences in connection with the drafting of specifications.

*The Chairman*, in closing the meeting, thought that the innovation had been highly successful. The suggestion to hold a lunch-time meeting had been fully justified.

A hearty vote of thanks was accorded to Mr and Mrs H. R. Murray Shaw for the buffet luncheon, and to the Rayon and Silk Association for the use of their premises.

## Lancashire Section

### The Selection and Training of Operatives in the Textile Industry\*

By HAROLD ROSTRON, B.Sc.

The question of the supply of operatives for the textile industry has for some time seriously perturbed employers. The lean time through which the textile industries have passed is so well known to all as to need no further mention, but it is obvious that it has discouraged the entry of labour into the industry. The setting up of new industries in areas in which originally the main activities were textile has resulted in the attraction of many workers with textile training and has absorbed labour that would, under normal conditions, have been absorbed in the textile industries. There is now abundant evidence of a shortage both of trained operatives and of new entrants. This has been investigated by Sir Cyril Entwistle, M.P., and Mr George Tomlinson, M.P. It will be conceded immediately that there can be little or no effective selection of labour for any industry unless the available supply exceeds the demand.

When such conditions obtain, employers are forced to consider the training of the only labour that is available and training them becomes the first and immediate problem of the management. Normally, training should follow selection. The placing of workers into a job needs first an analysis of the requirements of the job. The workers' abilities must then be investigated in order to find out how far these requirements can be met.

In textile work there is a major demand for manipulative ability and this is the first essential requirement. In the early days of the cotton industry child labour was employed for cheapness. Later the advantage of securing children at an early age so that their natural dexterity could be detected and developed by practice was realized. Few of the people concerned in the employment of

---

\* Abstract of a lecture before the Lancashire Section of the Textile Institute on 22nd March 1941.

labour have known of the phases of muscular development, particularly in the hands and wrists, and of the relations between the development of the lighter accessory muscles and of the fundamental or basal muscles. The lighter muscles can be developed in the young and this fact is utilized in the teaching of the piano or violin to children rather than postponing instruction until a more mature age is reached. But such early specialisation tends to warp the general development of both brain and body and to restrict the employment of muscles and nerves to certain parts of the body only. Physical training during school life can be employed to exercise the lighter muscles and develop dexterity and manipulative ability with greater all-round benefit than specialized training, particularly when the long view is taken and post-childhood employment is under consideration. Physical exercises should include lighter accessory muscle training and it is an advantage if this training can be planned to encourage recreative occupations such as art-craft work both general and in its application to textiles. Interest in recreative work of these kinds provides a refreshing complement and even an antidote to monotonous and repetitive work. It stimulates the desire to do things as well as to appreciate beauty and skill in work outside one's own ability.

Textile work in general calls for special requirements peculiar to the industry. Among these is fitness which should be both real and positive. The certificate of the visiting factory medical officer was usually to the effect that the person examined is not unfit, and it had thus a negative character. The examination should rather be directed to such things as vision, which should be accurate and acute, coupled with this should be rapidity of response to external stimulus. Intelligence should also be assessed and it is desirable that this should be above the normal.

It must not be forgotten that the best attempts to select operatives can be utterly defeated if there is no honest application of abilities. Ability and intelligence tests conducted in the course of selection of operatives usually encourage extra competitive effort specially whipped up for the occasion. The candidates' performance after selection may, in the absence of incentive to maintain the best effort, be of a very much lower grade.

Every possible effort should be made to encourage interest in the work generally and there should be a keen desire to know more than the particular part of the work on which the operative is engaged. To have this extra interest and knowledge reduces the tedium of the job to a greater extent than most people realize. This is the point at which industry makes close contact with technical education—two of whose services are to impart information and to cultivate intelligent interest.

Frequently it is found that technical education is a frightful bogey to many young textile operatives because it involves attendance for several years at evening schools. Local education authorities have provided excellent courses of technical instruction for those who aspire to the higher posts such as those of overlookers, head carders and managers. On the other hand, the technical training of textile operatives is still very much in the embryo stage. In the whole area covered by the Union of Lancashire and Cheshire Institutes there were presented for examination in 1939

474 candidates in Senior spinning and 55 in the Trade Course

905 candidates in Senior weaving and 91 in the Trade Course

or nearly 9 times as many students in Senior Spinning and nearly 10 times as many in Senior Weaving as there were in the corresponding Trade Courses. Yet the relative proportions of operatives' jobs to higher jobs greatly exceed the inverse ratios of these figures. Trade courses should be much more generally encouraged.

The final demand on the operative is skill in the work to be done and this is the ultimate object of training. The craftsman's technique must always be acquired *in the works* and is usually partly taught to new entrants by experienced employees. A training shed is ideal for the training of entrants to the industry. The operative's natural abilities must be brought out by influencing the mind and character of the young operative rather than by continued oversight and correction for a period. This is true education as opposed to the too common conception of education judged by examination successes in acquired knowledge and by the efficiency of the school in comparison with similar educational institutions. Where the idea of the training shed has been fairly tried the management and executive staff are fully convinced that there has been a consequent improvement in the quality of the work and in the tone of the factory.

The question may well be asked as to the necessity to the cotton operative of intelligence and the development of mind and character. A fairer question is: "Does training in intelligence, mind and character, make better textile operatives?" The answer to this is emphatically in the affirmative for it has been proved by experience. The Day Continuation School System has undoubtedly produced better operatives in every industry to which it has been applied. It certainly makes better citizens and the President of the Board of Education has envisaged the wide adoption of such a system as soon after the war as possible. The production by education of a more thinking and alert people generally will raise the intellectual level of new entrants into industry. This applies particularly to the textile industry, especially if it is true that a leading cotton employer of a couple of decades ago alleged that the Lancashire Cotton Industry needed a population of helots to man it.

Hitherto objection to a national system of part-time day continuation education has been urged by some employers on the ground that industry cannot afford to adopt it and that dislocation of the organisation is caused by the withdrawal of young labour from work for two half-days per week. Some firms, however, have not only declined to deduct wages for the time spent in the day continuation schools, but have actually borne the cost of the schools, they argue that they cannot afford to dispense with the school. The President of the Board of Education hopes to see part-time schools provided and run by local education authorities and under that scheme no direct charge will be incurred by individual firms. If the textile industry will accommodate itself to the employment of operatives who have passed through day continuation schools, it will get an increased supply of improved labour. Several industrial concerns have reaped considerable benefit in this way even though the work their operatives have to do is in many cases more monotonous than the jobs in the textile industries.

When the selection of applicants for work is possible the employer needs some method of avoiding the costly process of actual trial as a first selection to determine suitability and fitness of the operatives for given jobs. Head Teachers' reports and testimonials are usually too general to be of much assistance and the head teachers cannot reasonably be expected to know much of the technical requirements of the jobs for which they have to recommend the pupils who are leaving their schools. Similarly the foreman or manager cannot be expected adequately to assess on an interview alone, the natural abilities of the applicant for work. Selection can be aided by psychological analysis of the candidates but the layman has not the knowledge and skill which are necessary to conduct the analysis, this is work for the expert and the same applies in the interpretation of the results of the tests applied. Furthermore few employers can translate school reports into terms of ability and suitability for the work for which they have to find operatives, and the employment of the trained psychologist is warmly recommended. The intuitive appraisal of ability,

in which some employers excel, is valuable in the selection and engagement of labour and its value increases rapidly as it is supplemented by scientific and other evidence. It is agreed that there is insufficient work in the ordinary textile mill for a full-time psychologist, but he could be engaged to do the work for a number of mills in a district just as in the case of a certifying factory doctor.

## TWISTLESS AND LOW TWISTED YARNS

By Mr A. DRAPER, at Bolton, 3rd April, 1941.

Twistless yarn is not a very modern development. The idea is quite old and has exercised the minds of inventors since 1873, when a patent was taken out for an invention to produce ribbons or rolls from the down of birds, mixed with wool, and bound together by a paste or binding agent. Since that time, various processes have been developed to make twistless yarn, and considerable progress has undoubtedly been made.

An examination of conditions which must be fulfilled in the production and use of low twist and twistless yarn will best convey the aims of the several inventors.

They are as follows —

- 1 The yarn cost must be competitive with that of yarns produced from other fibres
- 2 The yarn must weave without difficulty
- 3 It should be capable of being used in ordinary looms without expensive additions thereto
- 4 To simplify subsequent processing only adhesives which are capable of being removed by ordinary finishing processes should be used
- 5 The fibres should be laid parallel, or nearly so, in the yarn, so that the maximum lustre will be obtained. The cotton chosen for this work should be suitable for mercerisation
- 6 To get the best results, the fabrics produced from twistless weft should be of the types where weft predominates, as for example, in figured or plain constructions. Fabrics so produced will not have the high lustre of rayon but should closely resemble real silk in appearance
- 7 Special attention should be given to finishing. Particularly helpful are such finishes as "crease resisting" if the fabrics are intended for dress materials. Mercerisation, of course, is indispensable if lustre is required

### Processing

Briefly the methods employed are along the following lines.

First, long-stapled cotton with high mercerisation value is chosen so that the binding effect of adhesive is assisted. A yarn is produced, preferably of the combed type, with the minimum amount of twist inserted. Following this, the yarn in the form of an open wound cheese is sized or treated with an adhesive substance in readiness for the next operation, which is detwisting. The adhesive must be plastic.

If a cheese is used, the usual method is to employ a doubler or similar machine to untwist the yarn which is then wound on to a pirn or bobbin ready for the shuttle. If rewinding is necessary, care should be taken to balance the twist inserted as the yarn is being wound off the pirn. The build of the pirn and condition of the yarn should be such as not to cause difficulty in weaving.

This sizing method has certain disadvantages which will now be described. It is a well-known fact that yarn from the same mules or ring frames spun at the same time, may vary in turns per inch because of slack and tight bands,



varying diameters of bands and the variations between spindle wharves. It therefore follows that some cops will contain more than the nominal turns per inch, and some less.

When untwisting takes place the same variations are introduced, and it may well be that some ends containing low twist will receive more than the calculated detwisting. This may occur if tight, thin bands run on undersize wharves. Instead of producing twistless yarn, this chance combination may result in a few turns being inserted in the reverse direction.

These variations, and the costly method of production, first directed attention to the possibilities of producing a yarn which had the same qualities—high lustre after mercerisation and greater fullness—and yet was cheaper and more satisfactory to produce. After considerable thought it was decided that the point at which lustre and fullness began to diminish must be determined. After considerable research it was shown that providing a yarn contained twist not exceeding 1.5 times the square root of the count, very little difference was discernible in the finished fabric. A variety of cotton with a high mercerisation value and long staple was then chosen. In deciding on staple length, the theory that cotton of 1 in. staple would have a low binding value with 1.5 turns per inch was used as a guide, and that if cotton could be obtained having a staple of 2 inches, there would be a greater chance of success with 3 turns per fibre.

From this preliminary work was evolved the idea of spinning yarn on ordinary cotton machinery with slowly revolving spindles, which would be capable of high production. It will be readily seen that 16's counts spun on spindles revolving at 7,500 r.p.m. with 16 turns per inch, would not be so productive as spindles spinning the same count from long staple cotton with 6 turns per inch running at only 3,000 revolutions per minute.

Considerable work has recently been done in this direction by the Shirley Institute in the production of cotton fabrics as substitutes for linen.

The lecturers' firm has had the honour of producing commercially these fabrics for the various services, and it is suggested that this is only the beginning of a spate of new uses for cotton which should continue after the war. As a field for research, work on these lines is strongly recommended.

To return to the use of low twisted yarns, it has been found that exceptionally low twisted yarns can be woven on ordinary looms without special additions if the weft is moistened with water containing suitable penetrating agents and antiseptics.

For the manufacture of twistless yarn, by what might be termed the sizing method, the yarn selected should preferably be of the combed type, because of the high degree of parallelism of the fibres and the great regularity of count. Twist runs into the thinnest place in any yarn, and the greater the variations over even short lengths, the greater will be the difficulties in subsequent processing. Further, the yarn should not be too softly spun, or stretching will take place in winding on and off the package.

If the yarn is wound on cheeses open crossings are necessary so that the size will penetrate readily. Open windings will also facilitate drying, and perhaps, most important of all, will prevent sticking during unwinding. There is no need to describe the various types of cheese winders for this purpose.

After the cheese has been thoroughly dried in a special oven, a weft doubling frame can be used for detwisting the sized yarn. The size on the yarn must be rendered plastic, so that the twist can be removed, for dry yarn so processed would give a yarn unevenly untwisted. The softening process consists of damping or steaming the yarn by passing it backwards and forwards between rollers or jets in a manner which recalls the gassing process.

Suitable revolving guides which will not accumulate surplus size are necessary, and brushes or doctor knives are required to present the yarn in suitable form.

If possible, a slight dusting with finely ground powder will complete the requirements, and the yarn is then ready for detwisting. Revolving yarn guides are necessary to prevent sticking. Drying of the yarn by means of warm air completes the treatment.

The spindles should run at 3,000 to 5,000 r.p.m., according to the count of the yarn to be treated. To obtain good results, travellers should be of the round wire type, with dry stainless spinning rings. The build of the pirn should be such that the coils are widely spaced to prevent sticking during weaving, and care should be taken with the determination of the amount of untwisting which must take place, to allow for the twist inserted during weaving. This method is fairly costly, due to the number of processes employed and the small production obtained.

Weaving is not so easily performed as with ordinary yarns, and in many cases a slower loom speed is desirable.

The resultant fabric will have, after mercerisation, exceptionally high lustre, and it is possible to obtain high cover from the weft with the normal picks per inch reduced by as much as 20 per cent., which to some extent compensates for the higher cost.

It may well be, as previously indicated, that new uses for cotton fabrics will create a demand for the introduction of these types of weft, and when placed in competition with some of our dearer textile fibres, they will be cheaper, and may even give better results.

It is here, then, that the possibilities of further research lie, and considerable advance may be made in the future. The yarns produced may not be entirely twistless, but processing on the lines indicated will produce yarns with special features.

The production of low twist yarn on ordinary machinery is a much simpler proposition, and given a well combed, even roving, processing on the modern ring frame is straightforward. To get the best results, the use of long staple cotton is essential, and the drafting mechanism should be such as to produce the most uniform yarn possible. A simple and very effective method on a fine ring frame, is to use a light middle top boxwood roller which can be of fairly large diameter, and yet facilitate ultra close setting. The front rollers should be covered with the best chrome calf leather, and have the advantage of a first-class roller traverse motion to prevent roller damage and assist close roller setting. Here again the travellers should be of the normal wire type and used on mirror-finished rings.

The build of the pirn is important. The builder cam should be speeded up, and be of a suitable type to give wide spacing of the coils, to obtain a firm package for the shuttle. The twist which is exceedingly low can be inserted at a slow speed consistent with good economical production, and if kept in the region of 1.5 times the square root of the count or even below, will produce a yarn capable of being woven without difficulty and giving all the characteristics of twistless yarn, without some of the disadvantages. Yarns so produced can be doubled to produce folded yarns of special type for use as warps, and when used in conjunction with low twist or twistless weft, produce novel and pleasing fabrics.

A feature of some fabrics is their highly absorbent nature after bleaching, and here again is a field which may be exploited profitably.

Cloth strength in the direction of the weft in these fabrics is remarkably good in cloths with a plain ground, and in many cases it is equal to or better than the weft strength of similar fabrics containing ordinary yarn. Three important factors are mainly responsible for this result. First—the fibres are laid parallel and the cross-section of the yarn is not round but flat, and the yarn lies in the cloth like a ribbon. In this state the threads running in the warp direction offer considerable frictional resistance to the discontinuous lengths of fibre in the weft, and prevent slipping. Secondly—the fibres used are long and convoluted,

and when closely packed together, interlock, and contribute greatly towards the strength. Thirdly—when used as weft, the warp threads are subjected to less crimp, and the arc of contact of the weft threads is increased.

Although the country is at war, there are many of us who still have some time to think and plan new projects for the post-war period. It is hoped that thought may be stimulated by this brief survey of the production and uses of twistless and low twist yarns, which are destined to play an important part in future production of textiles and are well worthy of attention. Some inventive genius may find a simple and effective method of solving the remaining problems.

(Samples of low twist and twistless yarns and fabrics produced from them were exhibited.)

## Yorkshire Section

### INDUSTRIAL PSYCHOLOGY

By Mr L. UNGERSON (National Institute of Industrial Psychology)

A lecture delivered to the Yorkshire Section of the Textile Institute, at the Midland Hotel, Bradford, on 20th February, 1941. *Mr Masters* in the chair.

The term "Industrial Psychology" is an unfortunately high-sounding title for such an interesting subject, and one of the interesting facts about it is that it owes a great deal of its development to the last war. Wars do give a fillip to some things, for example in this present war more has been discovered about aerodynamics than would have been the case in such a short period in peace-time, and the last war had this effect upon industrial psychology. In 1914 the belief was that if employees worked 20 per cent of their time longer, they produced 20 per cent more output, but this was found to be inaccurate, and in 1915 the "Health of Munition Workers Committee" was formed. This body found that the shape of the work curve, i.e., the graph of output production, was always the same in shape. Output was the only means by which fatigue could be measured. When curves had been plotted it was found that after a steady working period at maximum production, fatigue was felt and output fell considerably.

To counteract this fatigue, rest pauses were introduced, and from a careful study of the work curve it was easy to see where these rest pauses should be introduced in the working period. In the case of monotonous jobs the employer was faced with the alternative of introducing more rest pauses or varying the work as much as possible by widening the operational field. As an example, girls were employed in a chocolate factory in putting chocolates into paper wrappers. The trays of wrappers, already arranged, were brought to the girl who was sitting at a moving band, from which chocolates were lifted into their paper cups in the box, and the completed box taken away by another employee. These girls became bored and output fell rapidly, but if the girl fetched her own tray of paper cups, filled it and put it away again, output was actually increased by 24 per cent because of the reduction in boredom.

The next few points may be classified under "vocational guidance." In choosing a suitable operative for a job, it had been realised that personal appearance and apparent alertness were not a reliable guide. A series of tests had been evolved which could be varied according to the type of work for which operatives were needed. The first of these was the intelligence test. Questions were given on paper with a variety of one-word answers printed beside them, the correct answer to be underlined by the candidate—this eliminates the difficulty of comparative hand-writing speeds—and for the whole paper given a time-limit was imposed. The test is based upon the ability to see the relation between two facts and to use that knowledge in other directions.

The mechanical ability test is, as its name implies, a practical test of mechanical ability, showing the amount of "mechanical instinct," the ability quickly to grasp the fundamental principle of any working machine which is apparently innate in some people. A third test is that of "choice reaction." A square box with a row of differently coloured knobs along the top has a window which, on the pressing of another knob, shows a coloured light. The corresponding coloured knob along the row at the top of the box must be pressed as quickly as possible and the reaction time is recorded with the number of mistakes. The latter is the more important factor.

Another test is that of "visual ability," the ability to watch a number of things at once. A slightly more involved instrument, consisting of a box with four "windows" behind which moving bands travel, is used for this test. On one of these bands are consecutive numbers which move throughout the test, on the others are marked (a) crosses, with occasional blank spaces between them, (b) parallel lines with a bulge in them, and (c) wavy lines with straight pieces here and there. The person undergoing the test stands in front of the box and, for example, when a blank occurs on the band bearing the crosses, says which number shows in the window. The test is built up until all four bands are moving at once and a record is taken of the number of mistakes made. In all these tests 100 per cent perfection is impossible, so they must first be tried on satisfactory operatives of many years standing in order to find the necessary standard.

The importance of these selection tests is nullified if we are still content to mix newcomers with skilled workers and expect them to "pick up" the job. The training of a new worker may be split into two parts (1) the mental training, and (2) the acquisition of mechanical skill.

(1) Mental Training. In the case of weaving, for example, the number of technical terms is very large. A course of systematic training has been built up and explanations of these terms are given, the general principles being shown on model machinery. Examples of all the possible faults, their causes and how to avoid them, are studied by the newcomers as part of their training, with the result that young girls are able to turn out work superior in both quality and speed to that of most of the old hands.

(2) Acquisition of manual skill. The quickest and easiest method of attaining manual skill is by making a study of the necessary movements. In order to do this it is best to make films of good operatives working at their normal speed, and exhibit the films in slow motion form. By this means comparisons may be drawn and a standardised sequence of movement taught to students. Economy of expenditure of physical effort is most important. General principles should be laid down with broad limits for individual characteristics such as left-handedness, and in the early stages of training speed should not be stressed as it is important to cultivate correct habits which entail the least amount of physical effort. One of the best means of constant instruction is by showing slow motion films while operatives are actually working their machines, and can keep looking up to make sure of the correct actions.

To sum up, the three most important factors, therefore, which make for the highest rate of output are —

- (i) Finding the right person for the right job (intelligence tests, etc.)
- (ii) Systematic training in methods based upon a study of the easiest and quickest way of operation
- (iii) Providing good equipment and working conditions

Mr *Masters* thanked Mr Ungerson for his very interesting lecture. He mentioned the traditional Yorkshire independence and its prejudice against innovations. He also asked if women became bored more quickly than men, and whether left-handed or ambidextrous people had been found to be more alert than right-handed people.

*Mr. Ungerson* said that in many cases extreme tact had to be used for the introduction of improvements and good must be done by stealth. It is generally agreed that women can endure monotony better than men. Monotony is best relieved by the introduction of variation. The unemployment problem often has to be faced after improvements in working conditions have been made. For example, weavers provided with ear plugs increased their output by 8 per cent because less fatigue due to noise was felt. Although some unemployment may be caused, improvements in working conditions and equipment must not be ignored.

Care must be taken not to base our estimation of another's boredom upon our own standard. An example of this is given in the case of girls employed in placing small pieces of mica into position in condensers. This was described as interesting work if the pieces of mica numbered less than eight—because it becomes automatic and needs no active thought, leaving the mind free for more pleasant subjects, but if the pieces of mica numbered over ten, the job became "boring" because it was necessary to concentrate upon the counting of the pieces to the exclusion of everything else.

*Mr. Hall* observed that music had proved helpful in such cases.

*Mr. Ungerson* held that music should only be played when concentration is not essential to the work in hand.

*Mr. Masters* asked what type of music had been found suitable to play to assembled workers.

*Mr. Ungerson* replied that this depended upon the taste of the workers themselves, although dance music was acceptable to the majority.

*Mr. Shann* had found many employees unwilling to take on a strange job. They would rather stay in a rut.

*Mr. Ungerson* explained that they are afraid of failure and would rather stick to a monotonous job in which they feel secure.

*Mr. Masters* pointed out that in these monotonous jobs the workers watch the clock the whole time and work solely for their wage. In other cases there is a definite interest in the work and employees do not mind working overtime. How is it possible to achieve equity?

*Mr. Ungerson* There are not enough interesting jobs to be had so these cannot be evened out. The only way to make every job interesting would be to go back to the old craftsmanship methods, discarding mass-production altogether, but the standard would be considerably lowered. It may be that monotony will have to be endured on an increasing scale for the sake of a higher standard of living.

Mention was made of the reluctance of employers to grant rest pauses and the fear of employees to take them in case of a drop in wages.

*Mr. Ungerson* said that the textile industry was particularly conservative in this respect and it was thought that the reason for this lay in the fact that the textile industry was originally an industry practised in the home.

*Mr. Robinson* said that in the case of weavers, women liked to finish pieces and felt that they had earned more if three pieces a week were finished than if one piece took four days, although such was not the case. He asked how the character of an individual, influenced by heredity, temperament and environment, could be judged at an interview.

*Mr. Ungerson* The subject of interviewing itself is a very wide one, but one of the first necessities is to write down on paper before the actual interview those characteristics most suitable for the job in question. A scale could be made out against each one; say, when interviewing a commercial traveller, against "sociability" the letter (a) might denote "very good," (b), "good amongst people of his own class," (c) "fair mixer but shy," (d) "aggressive," and so on.

This must be filled in during the interview, and what may be termed a "halo" effect guarded against. This is the natural tendency to over-rate in the possession of one's own deficiencies, and is an unconscious self-deception.

*Mr Hall* asked about the influence of fatigue in mechanical ability and other tests, and it was explained that the testing period is so short that fatigue is negligible. A standard amount of practice is given, followed by two minutes rest, and half a minute's run on the testing machine, but speed is a factor in all these tests as speed usually shows a clear head.

*Mr Robinson* had found one class of employee willing to cut production because if maximum output was maintained "too much" wage would affect income tax payments. Married women studied their own convenience before that of their employer and were not so concerned about wage-earning.

*Mr Ungerson* agreed, and added that this applied also to young girls who gave their wage to their mothers in any case.

*Mr. Jones* stated that operatives worked better at a flat rate provided a high quality was maintained.

*Mr Robinson* said that rest periods had been introduced early in the day at about 8 a.m., because when workers started at an early hour their breakfast was often scanty and fatigue was felt early because of lack of food. This was unfortunate because the break came at a time when they should be working steadily up to a peak production period, but the need for food over-ruled this.

*Mr Ungerson* The rest period is more valuable if it is an accepted rule and is set apart as a time in which every individual can do exactly as he pleases. Some girls enjoy dancing to a gramophone, which is good recreation for sedentary workers.

*Mr Masters* closed the discussion with thanks to *Mr Ungerson* for an extremely interesting lecture and enlightening discussion, and called upon *Mr Robinson* to propose a vote of thanks. *Mr Robinson* was seconded by *Mr Kohner*.

## "RAYOLANDA"

An exhibition was held in Bradford from May 26th-29th, to introduce to the worsted and woollen sections of the textile industry a new synthetic fibre—"RAYOLANDA" (regd)—which is made under a Courtauld patent.

"Rayolanda" is one of those fibres which have been somewhat incongruously described as "animalised," which is used to indicate that the fibre has an affinity for the dyestuffs used for the dyeing of wool. Those who follow the patent applications as a reliable indicator of research activities are aware that a large amount of research has been conducted in this field during recent years, as evidenced by the fact that there are a matter of 500 patents which incorporate as a main or subsidiary claim the production of a fibre with affinity for the dyestuffs used for wool. There are, however, at the present time, only two of these fibres which have reached commercial production, even on a limited scale, thus illustrating the very wide gap which frequently exists between discovery and commercial production. "Rayolanda" is one of these two new synthetic fibres which has been in course of development during the past four years. Within this period it has passed from the laboratory bench to the pilot plant, followed by prolonged spinning, weaving, knitting, dyeing and finishing trials, to the ultimate consumer for wearing trials, arising from which no complaints have been received.

Limited production is now proceeding on a large scale plant in  $4\frac{1}{2}$  denier, 6 in. and 2 in. staple. Present circumstances do not permit of production in other

deniers, though it is apparent that there will be an equal, if not greater, future for "Rayolanda" in  $1\frac{1}{2}$  denier for cotton spinning machinery.

"Rayolanda" is produced on a cellulosic basis and contains no protein. It has several outstanding properties which include a full, distinctive and pleasing handle, coupled with a widely controllable affinity for dyestuffs of all classes, which enable tone-in-tone or heather effects to be obtained by a single bath dyeing process—effects which were hitherto only obtainable in 100 per cent wool fabrics by colour blending and weaving. This presents to the merchant and manufacturer the great advantage of permitting him to keep his stock in the grey and to have it dyed in specific colourings, as and when required.

"Rayolanda" is not offered as a substitute fibre for any existing fibre, but rather as a supplementary fibre to be used in blends with existing fibres, because it is not recommended, in its present stage of development, to be used in 100 per cent worsted spun yarn. The policy of its present production, which is necessarily a limited one, is to place in the hands of the British textile designers a new and unique tool, thereby giving them a preferential start in the production of new and attractive cloths for export markets, since novel and attractive effects may be obtained by a single bath dyeing process, either in piece or in folded yarn form—the latter being specially applicable for knitted fabrics of attractive design for outerwear, such as dresses, pullovers, scarves, etc.

It must not be expected that "Rayolanda" in its present stage of development is free from defects. The experience gained in the development of established synthetic fibres shows that it would be unreasonable to expect it. Efforts to remove these are continually being made with the patient co-operation of the users.

The dyeing of the fibre in conjunction with other fibres provides a most interesting study, and a brochure has been issued containing very detailed instructions regarding the possible varied effects obtainable with all classes of dyestuffs.

# THE JOURNAL OF THE TEXTILE INSTITUTE

Vol XXXII

JULY 1941

No 7

## PROCEEDINGS

### NOTES AND ANNOUNCEMENTS

#### SUMMER MEETING 1941

The Summer Meeting, which was held at the Midland Hotel, Manchester, on Wednesday, 18th June, 1941, was a most successful function. Because of the difficulties of war-time it has not been expedient to have the usual Annual Conference since 1939 and some considerable time had elapsed since members had had an opportunity of meeting together. The excellent attendance, therefore, at the Summer Meeting was very gratifying, and was due in no small measure to the helpful and energetic co-operation of section officers and members.

There were present a hundred and fifty members and guests and Mr G H Thompson, President of the Institute, presided over the assembly. The guests included Sir Percy Ashley, Mr T Ashurst, H M I, Mr P F Burns, Dr C J T Cronshaw, Dr J E Myers, Mr J W Nasmith, Mr J Noguera, Mr J R Scott and Mr E Raymond Streat. The programme commenced with a luncheon which was followed by the presentation of Institute honours. The Honorary Fellowship of the Institute was conferred on Mr Fernando Casablanca, of Barcelona, in recognition of his outstanding work on high drafting, but as Mr Casablanca was unable to be present the award was received on his behalf by Mr J Noguera. Mr W W L Lishman, of Todmorden, Honorary Treasurer and Vice-President of the Institute, was presented with the Institute Medal after being introduced by Dr C J T Cronshaw.

The Mather Lecture which followed was delivered by Professor J B Speakman, Professor of Textile Industries in the University of Leeds. The title of the lecture, which is printed in full in the Transactions Section of the *Journal*, is "The Chemistry of Wool and Related Fibres". Those present will long remember the masterly way in which Professor Speakman gave his address.

Following the lecture those in attendance had afternoon tea at the invitation of The Textile Institute, after which there was an opportunity for members from the various sections to meet together informally.

A full report of the proceedings follows.

#### Speech of Welcome by the President of the Institute

Mr G H Thompson welcomed those present at the luncheon and said: "It is my pleasure, Gentlemen, as President of the Textile Institute, to give you a hearty welcome to our proceedings to-day. The Council, the Officers and I are all gratified to find that so many of you have found it possible to spare the time to join us in what one might term a rationed conference, for it is rationed both in time, in fare, and even in speeches. Here for an hour we can get away from the things that obtrude upon, and unfortunately in some



cases obsess our thoughts. We enter, as it were, a wider orbit ; we cease to revolve around a nucleus , we can forget the telescoping of business , we can even forget fixed margins and rising costs. Later we might have to become good microscopists to find a profit, but for to-day let us forget whether combines are growing or whether this, that or the other is the best or proper thing. We are in Manchester, the sun is shining, we are alive. When I look to my right and to my left and see the galaxy of orators about me, what a pity it seems that the maggots gnawing at the mind of a darned paper-hanger should act and curb our speeches. Some other time we hope will give us our chance, but to-day we are fielding, to-morrow or the day after, we hope to bat.

" It is not my intention to cover the ground of the Institute's work , you are well aware of its activities. I should rather like to picture it as an impersonal machine, where the giant wheels of the organisation run smoothly round and cogs fit with constant precision. I may be wrong, but I look on the Institute as a tremendously efficient organisation which goes driving smoothly on without moods, without fears and without haste, and even without showing any signs of weariness. Its President is only a bird of passage, but even so, a feeling of tranquillity and satisfaction can come his way, and, with every member and associate of the organisation, he can enjoy unbounded enthusiasm, for in his mind he knows that the work done is not a meaningless effort. It is intended to be, and is, a real service to the world. Prestige and confidence grow apace. They are achievements that cannot be hurried, but a host of men have worked hard and are willing to go on working for they believe that their efforts are worth while. During the past years we have lost by death, two gentlemen who were staunch workers. I refer to the passing of Major F R McConnel and Mr John Crompton. Both, I believe, were past Presidents, men of sterling quality, and charming manner. We were sorry to lose them, but the work of the Institute is for us who yet are spared. A great many men of good will and good faith have resolved to make it their life's work.

" Gentlemen, I welcome you and hope that our assembly will prove profitable to all "

#### **Toast to the Guests**

Mr F Nasmith, an ex-President and the acting Secretary of the Institute, in proposing the toast of " Our Guests ", especially referred to the presence, amongst others, of Sir Percy Ashley, the Cotton Controller, who had been a member of the Institute for many long years and who had on every occasion assisted the work of the Institute to the best of his ability and had done an enormous amount of work in this respect , Mr. Raymond Streat, the Chairman of the Cotton Board, whom everyone had known for so many years as the Secretary of the Manchester Chamber of Commerce , Mr T Ashurst, Director of the Cotton Spinners and Manufacturers' Association , Dr J E Myers, the Head of the Manchester College of Technology, whose father, Professor Wm Myers, was well known to all who participated in the work of the early days of the Institute—it was pleasurable indeed to see Dr Myers in the position he held to-day, and also to welcome him to a function of the Textile Institute, for which his father worked so long and so assiduously , Mr P F Burns, H M Inspector for Textiles , Dr C J. T Cronshaw, President of the Society of Dyers and Colourists and a Fellow of this Institute , Mr. J. Noguera, who attended as the representative of Mr Fernando Casablancas, who had been awarded, as probably all knew, the Hon Fellowship of the Institute , Mr J R Scott, of the Ministry of Information ; and Mr J. W Nasmith, who was awarded the Hon Fellowship a number of years ago for his work in connection with the development of the Comber that bears his name.

Responding to the toast, Mr Raymond Streat, on behalf of the guests paid a special tribute to the assistance rendered to the Institute by Sir Percy Ashley,

who was President of the British Standards Institution, and who conveyed the greetings of that body to the members of the Institute. He also referred to the extraordinary energy and vigour which Mr Frank Nasmith had always devoted to the furtherance of the affairs of the Institute. In conclusion, he expressed a wish that it might not be long before the Institute could resume its usual course of holding its Annual Conferences when the Mather Lecture could be delivered amid the sunshine of peace

#### **Award of Honorary Fellowship to Mr. Fernando Casablancas**

After the luncheon the award of Institute honours was made, and on conferring the Honorary Fellowship on Mr Fernando Casablancas, the President said:

"It is my pleasure to introduce to your notice a few of the salient points of what has become the life work of a gentleman whose name during the last decade or so has become so well known amongst textile men generally and cotton spinners particularly. I refer to the work of Fernando Casablancas, a Spanish national, whose name has become synonymous with high drafting of fibres. Lewis Paul or John Wyatt a little over 200 years ago (1737) were the first to use rollers for drafting or spinning, and during this interval of time the names of men are legion who have experimented and made slight improvements, but the principle of successive pairs of rollers remained the same. Without going into the technicalities of the impossibility of ideal drafting by successive rollers of various lengths of fibres as found in all commercial cotton, it has fallen to the lot of Mr Casablancas to show us a better way of drafting. It traverses the old ideas only so far as to retain the first pair and the last pair of rollers. Positioned between these two pairs of rollers is the Casablancas apparatus. Briefly, this consists of endless leather bands or traversing aprons properly tensored to suit the average staple length. The bottom or lower apron is positively driven, and the upper band is carried in a cradle which moves by contact with the bottom apron, while the material being drafted is lightly held between these bands. The whole mechanism works with an easy smoothness, and the control of the short fibres is outstandingly efficient. That is not the whole story, but to you who know it so well it is sufficient for my purpose to-day. Here we have a principle that can produce a tolerably good yarn from a much higher draft than was possible hitherto, thus cheapening the cost. Alternatively the apparatus can be used with lower or normal drafts to make yarns of greater uniformity, yarns almost as level and regular as the slivers from which they are made. That, gentlemen, is the invention. What of the man? Fernando Casablancas was born in 1878, and he was brought up as a textile mill man. His interests have always been essentially technical. He, personally, seems only to have cared for and striven with dogged determination after the technical merit of his achievements, and although his name has been famous throughout the world for the last 20 years, he had been working and pegging at it from the beginning of this century. Mr Casablancas is a man whose inventions have brought him not only honour but much commercial reward and to-day he is the head of a number of important firms in different branches of the Textile industry, but even with these toys to play with, much of his time is spent in his experimental factory and workshop. Mr Casablancas has taken out about a hundred patents, some of them being very ambitious ones. Some of you will remember a machine being on exhibition many years ago made by the German firm of textile machinists, Hartmann of Chemnitz—a machine which spun yarn directly from draw frame sliver. This was a Casablancas machine produced under licence by Hartmann. I just mention this to show that he has paid some attention to other textile matters, yet it is in the drafting of fibres that his interest has been mainly absorbed. At the

present time there are about 30 million spindles working on the Casablanco system and whichever way one looks at it, whether it is the production of a cheaper or a better yarn, this means a substantial contribution to the trade. I am not going to try to give it a capitalized value, but it must save the industry an enormous annual sum. Mr Casablanco has been honoured particularly by the men of his own country who have awarded him many distinctions. The industrial Spanish town of Sabadell has given his name to one of its principal streets. To-day the Textile Institute, under its charter, is to award him its Honorary Fellowship, an honour that is reserved for inventors whose work is outstanding and of major importance. The award has only been made on four previous occasions — To Mr Horace Lowe for the development of Mercerising, to Mr C F Cross for his work on Viscose, to Mr C F Topham for his invention of the Centrifugal Spinning Box, and to Mr J W Nasmith for the Comber that bears his name. To-day another name is added to that list, and but for the problem of travelling during war-time, Mr Casablanco would have been happy to be here, but Mr Noguera, who has been



MR F CASABLANCO

Awarded the Hon F T I, in June, 1941

associated with him in his work for many years, is to act as his proxy. Mr Noguera, will you, on behalf of Mr Casablanco, accept this document and tell him that men of goodwill wish him a measure of long life and contentment?"

Mr J Noguera thanked the President for the high honour which had been conferred on Mr Casablanco and in reply read the following letter from Mr Casablanco:

"Members of the Textile Institute,

"I cannot be with you personally, but I am glad I can at least convey to you through my friend, Mr Noguera, how happy and moved I am at the news that the Textile Institute is awarding me an Honorary Fellowship. Truly, I never dreamed that a distinction such as this, which I shall value so much, would ever be conferred upon me.

"During all my working life nothing has ever given me so much genuine pleasure as the acknowledgment of my work by other technical men whose thoughts and interests, like my own, are in the Textile industry. You will therefore understand my feelings on receiving such a generous recognition from the Textile Institute which is essentially composed of men born and bred in the greatest textile centre in the world.

" It seems indeed, a long time since the introduction of my drafting system and its first impact with the spinning industry. A draft three times higher than usual on the spinning machine, the suppression of one passage of speed frames (thus recklessly missing one doubling operation), the cheapening of cotton mixings by the addition of shorter-staple material. These things were then, to many people, pretentious and, technically, almost blasphemous suggestions.

" I mention this here, not only without malice, but looking back with satisfaction in the thought that I may have contributed in some measure to the present better appreciation of the drafting processes. On the other hand, I well understand I could not hope to expound my drafting methods without considerably ruffling the 'placidity' of established practice and equipment then existing, not only in the cotton spinning mills, but also in the engineering shops where the machines for them were made.

" The spinners were certainly the first to be interested, and I must here acknowledge gratefully their constant help and encouragement, especially during the initial years when large scale installations of my drafting apparatus for different types of production and under different conditions of work were first being made.

" I feel I also owe much to the many technical men whom I do not know and who, without knowing me, have for a long time applied themselves with keenness and competence to explaining and popularizing some of my theories on the drafting operation.

" Members of the Textile Institute, my opinion of your Association is high, and by your decision to bestow upon me your highest honour, you are making me very proud indeed. I thank you most sincerely for this distinction which I will dearly treasure all my life."

#### **Award of The Textile Institute Medal to Mr W. W. L Lishman**

Dr C J T Cronshaw introduced Mr Lishman to the President, saying

" It is to-day my great privilege to commend formally and on behalf of the Textile Institute, Walter William Lancaster Lishman for the award of the Institute Medal. In the award of this medal to him the Institute sets an imprimatur upon not only great technical distinction, but upon a devoted and indeed almost passionate service in the cause of the Institute itself. Mr Lishman cannot talk for long without talking about the Institute, it is part of his life and being. Mr Lishman is the discoverer of the bleaching process which half bears his name—the 'Lispro' process, and is the inventor of the Lishman dyeing machine for dyeing cotton warps with a low degree of tension. He was, when pioneering was difficult and to some extent unpopular, a pioneer in the kier-boiling of cotton yarns, and he was instrumental in introducing this process into Ireland. These are great achievements, but even they are but outward manifestations of the numberless refinements in technique which he has contributed and which have gone to build up and mould the technique and practice in an industry in which Mr Lishman has served so proudly and so well since when as an apprentice he entered in 1880 the warp dyeing trade in Bradford. Gifts such as Mr Lishman's seem ever to thrive and become intensified if their early atmosphere can chance to be in Yorkshire.

" The Institute Medal goes to a man who has seen within the compass of his own practical life the revolutionary change from natural dyestuffs to a vast synthetic range to-day. The train of problems in dyeing technique, arising during the close of one era of technology and the full development of another era, fell within the sphere of endeavour of Mr Lishman, and you can well understand that only the Recording Angel could give with completeness an account of Mr. Lishman's achievements. Nor do they need cataloguing, they are to-day an integral part of the present technology of dyeing.

" Mr Lishman had, moreover, gifts of leadership, and in 1894 he went to Todmorden to start his own business, in which he still maintains an active

interest and in the warp dyeing trade generally. Perhaps he is the oldest active dyer in the trade to-day, and that to him is less a description of his occupation than a title of some distinction. Nor would his friends wish him to consider it otherwise.

"It is said that only the busy people have time for other things. This is abundantly true of Mr. Lishman; he has I should guess packed as much first class voluntary service into his life as may well be. I have spoken about his service to this Institute; there is also his ungrudging service to the dyeing trade generally—he must have served upon nearly every Committee that was set up, and he has given freely of his ability and time to the Town Council and all manner of local affairs in Todmorden.

"Mr. Lishman has preferred to live his life in the neighbourhood of his business at Stansfield Hall, Todmorden. Nor is he the man, I believe, who must work in one place and live in another.

"His hobbies are his work, his garden and a special concern for his roses. Mr. Lishman was fortunate and was born with an eye for colour, especially for



Mr W W L LISHMAN

Awarded The Textile Institute Medal, in June 1941

a fine shade discrimination, and some dyers believe—though I cannot vouch for this—that his ability to match shades has some basis in astrology and that he was able to feel the rays from the patterns. I do not say I share this view, but I can well understand the high degree of skill which seemed to others to require some magic power. Nor did Mr. Lishman entirely ignore all the pomp and circumstance and panoply of power. In the spacious days, it was his practice to drive from Cornholme to Todmorden Station in a carriage and pair.

"Mr. President and Gentlemen, I commend for the award of the Institute Medal, Mr. Walter W. L. Lishman, for his great distinction and performance in the industry, and for a life of great service to the Textile Industry, to this Institute, and to his fellow men."

Mr. Lishman received the medal from the President and replied.

"Mr. President, Dr. Cronshaw, Ladies and Gentlemen,

"Since your President and the Hon. Secretary informed me that it was the intention of the Council to present me with the Textile Institute Medal for services which I have rendered to the Institute and to the trade, I have been considering how I could adequately thank the Institute and I find it difficult

to express myself sufficiently for the great honour I have received. All I can say is, thank you very much indeed. You can be very certain that I shall always prize this Medal, and whenever I look at it I shall remember that I had the esteem and confidence of my fellow members to the extent that they have considered I am worthy of the Medal. I shall safeguard it and I shall pass it on to my family to indicate the regard in which I was held by many people of my day and generation. Again many thanks.

"Mr President—with your permission I should like to say a few words as to what in my opinion the Institute stands for and something of the work it is doing for the textile industry and the country at large. It is well known and recognised that the work of the Institute is done voluntarily by a number of men who, especially in these days, have many other duties to occupy their time. In my position as your Hon. Treasurer I have had many opportunities of observing the work of the Institute and I have recognised the usefulness of this work as a commercial man. I would like to convey to this distinguished company of guests and members a thought that may help forward the valuable work that has been going on for a number of years, and a hope that this work will have far reaching results in the improvement and development of the trade of the textile industry when the war is over. I firmly believe that the industrialists have endeavoured to work in watertight compartments without giving much thought to the advantages that can be secured from those who are engaged in scientific research and investigation. For many years it has appeared to me that this isolationism has not only been fraught with many dangers, but it has been a deterrent to the progress of the industry and has prevented us from utilising all the advantages which are valuable to us in order to meet foreign competition.

"In my opinion, the time has now arrived when we should depart from this state of isolation in the industry and take full advantage of that considerable knowledge which has been, and is being built up. We do not take the same advantage of the work done for the advancement of the industry as do our competitors. In many cases they are able to commence where we leave off, and it is undoubtedly a problem as to what will be done in the way of post-war development, rationalisation and the like, after this present state of war is over. I am glad to know that the question of post-war development is receiving the attention of your Council, together with many other important matters that concern the industry closely, such as, for example, the recruitment and training of labour.

"In my opinion I believe the Institute, as it is now constructed, can be of enormous value to the industry at large. We are becoming more closely allied with all those movements which tend towards development, and I believe that later on a bureau of information will be set up which will be of inestimable value to both the employer and the employed.

"As your Honorary Treasurer I have often thought that what the Institute requires is co-operation and goodwill, and still speaking as your Honorary Treasurer, the point I wish to stress is that the Institute requires support both in kind and money to bring about the success which we all so much desire, and for which a number of men have laboured over many years giving their service voluntarily. I feel sure that I can count on the full support, of all those present to-day to attain these objectives."

## Textile Institute Diplomas

The following election to Associateship has been completed since the appearance of the previous list (June issue of the *Journal*) —

**ASSOCIATESHIP**  
GEORGE HELLIWELL

### EXAMINATION RESULTS, 1941.

The results of the Examinations held in relation to the Associateship of the Textile Institute, in May, 1941, at Bradford, Dunfermline, London, Manchester and Nottingham, have just been issued. The following passes are recorded —

#### Preliminary Examination: Essay only

S A Burbidge, Nottingham

#### Examination in General Textile Technology

J Cooper, Farnworth	P G Noble, London
S W Farrington, Spondon	D F Paling, Cossall
R Foster, Leeds	J Pemberton, Bolton
G W. Eisig, Manchester	Miss V F Waterhouse, Ilkeston
S W Greator, Manchester	J Willock, Manchester
J D Griffiths, Manchester	R Wood, Bradford

Names marked with an asterisk are of candidates who have now completed the qualification requirements in regard to the award of Associateship (A T I)

#### Examination in Analysis and Testing of Textile Materials

The following candidates were successful —

S H Carter, London.                      E C Harrold, London

#### Institute Membership

At the July meeting of Council the following were elected to membership —

G A Cookson, "Ibwe", Dakota Road, Claremont, Cape Town, S Africa  
(Factory Manager)  
J L Ingham, Wilson Bros Bobbin Co Ltd, 324, Royal Exchange Buildings,  
Manchester  
D N. Marvin, "Wendover", 64, West End Drive, Ilkeston, Derbyshire  
(Student)  
H A H. McGill, 60, Huddersfield Road, Oldham, Lancs (Director of Platt  
& Co Ltd, Oldham and Samuel Dodd & Sons Ltd, Oldham)  
G Phillips, 19, Gain Lane, Thornbury, Bradford (Woollen and Worsted  
Buyer)

#### Employment Register

The following announcement is taken from entries in our Register of Members whose services are on offer. Employers may obtain full particulars on application —

No 226—A T I, 36 years of age. Eight years' experience as Assistant Production Manager of Plant producing Rayon Staple Fibre City & Guilds Full Technological Certificate in Cotton Spinning Would prefer to go abroad

**TEXTILE FINISHING IN WAR-TIME**

By R J SMITH F.T.I.

[I.C.I. (Dyestuffs) Limited]

*Lecture given at the Textile Institute, Manchester, on 24th June, 1941*

This paper has, I fear, a most ambitious title and in fact unless I limit it to a relatively small number of the problems incidental to war-time conditions, it will take an inordinate amount of your time. Apart from considerations of such acute problems as the control of raw materials, limitation of supplies, diversion of goods to the war need and concentration of plant, a whole host of difficulties have faced the industry as a result of changed conditions and demands. It will be generally agreed, I think, that by comparison with 1914, we are far better served as an industry and we have available a wider range of replacement products (I deprecate the use of the word "substitute"), than we ever had during the years of the last conflict. Probably the chief difficulty has been the sudden change in the type of goods which many firms have been called upon to produce. Generally in the textile industry, any particular firm or associated group of firms, is accustomed to handle in a specialised way specific types of fabric or to carry out certain well-defined processes. Under war conditions such specialisation may be very undesirable and flexibility of plant and of personnel become all-valuable. It is greatly to the credit of the finishing sections of the industry that they have ably responded to the demands made upon them by the changed conditions and have attacked with success and vigour the many problems put before them by the call for war-time finishes and fabrics.

In the course of my normal work, I have been in the fortunate position of an observer of many of these efforts and some of the various problems which have come to my notice may be of interest to you. Particularly would I ask you to look upon these problems as I do, that is, as a potential source of ideas for post-war development and progress. Do not let us file away all these war-time expedients and experiences and forget them when peace and normal times return. Rather let us bear them in mind so that, when better times are restored, we may profit by them and add to the well-being and comfort of those who depend upon the industry for their clothing, their furnishing, and all those textile products which in peace time, play so great a part in promoting what is usually called, a high standard of living.

This view is not mine alone—following upon a recent piece of advice given to one firm regarding a method of effecting an economy in one of their processes, they wrote.—

"It is a pity that we have to be at war to make the industry think of substituting a product or a process, which in this case has proved better than the normal one. Production is speeded up, the plant keeps cleaner in operation, we use two-thirds less raw material than we did in pre-war days and the finish is fully maintained."

Of course it must be remembered that we are all more alive to such possibilities in war-time, since necessity is the mother of invention, but surely we ought to show the same readiness to try out new ideas in peace time, and I am afraid that many of us were not probably as willing then, as we are now under forced circumstances.

Some of the items which I hope to bring before you this evening are essentially the products of war-time demands. They are principally of chief interest in war-time but should be, in many cases, capable of adaptation with advantage after the war is over. Others are really modification of peace time processes to meet abnormal conditions, while others which I could discuss, are pure expedients—methods of overcoming shortages of materials or plant deficiencies. These, rightly or wrongly, I do not regard as being nearly as



important as the two former classes, for they are stop-gaps, even if, under present day conditions they have proved to be valuable stop-gaps

Probably one of the outstanding developments during the past two or three years, i.e. immediately prior to and during the present war, has been the attention paid to water-proofing. This particular finish is referred to in many Government specifications, including DTD 336A, DTD 448, LAG 1116E, LAG 1150D, E 1026, AM 792/NA, and, of course, in connection with T 500 fabric, otherwise known as "bluette". The demand of these and allied specifications, falls chiefly into two classes, (1) those calling for a durable finish free from wax and possessing high repellency, and (2) those which can satisfactorily be met by the use of a wax/aluminium salt finish. The increased demand for water-repellent finishes by the services can be traced to a variety of causes. The greater use of mechanised equipment under field conditions demands protection of the vehicles, etc. against weather, whilst aircraft require similar protection when grounded. The substitution of leather by webbing equipment and the use of cotton fabrics by A R P services under all conditions of weather have also increased this demand. As for the services themselves, the ill effect upon health of wearing wetted garments has been finally appreciated, and as a direct result, water-repellent fabrics are now demanded.

Obviously on those fabrics exposed to extremes of temperature a wax-proof is not likely to prove satisfactory. At low temperatures the fabrics harden and become so stiff as to be quite unserviceable. Similarly on fabrics such as denim or bluette, which may quite often need laundering, a wax-finish is not a practicable proposition, since laundering destroys the repellency. That a British product has been available since before the war, which has enabled a durable water-repellent finish free from all these defects to be produced, is a very satisfactory state of affairs. For those materials satisfactorily dealt with by the normal wax/aluminium process, several excellent proofing agents are available. Care is, however, needed in processing all the fabrics covered by the specification referred to, and whilst many firms habitually process such goods, other firms have been called upon, under stress of heavy demand, to carry out water-proofing treatments. At the risk of "carrying coals to Newcastle" a few hints may not be here out of place. Impregnation of the fabric by the proofing liquor must always be thorough. This may entail multi stage padding or the overhaul of impregnating ranges. However difficult the achievement of complete impregnation may be, it is to be remembered that on this initial stage the final success of any proofing process largely depends. Another point in the process calling for care and attention is the final drying. Low temperature drying is rarely, if ever, satisfactory. High final drying temperatures are essential if the best repellent effects are to be produced. If these two stages of the wax-proofing process are carefully providing the recommendations covering the application of this product are

So far as the durable finish (Velan PF) is concerned a great deal has already been published about this process. It may suffice to say here that providing the recommendations covering the application of this product are adhered to strictly, entirely satisfactory results cannot fail to be produced.

Arising out of proofed finishes one point of considerable interest has arisen in connection with the sewn seams of heavily waxed or oiled fabrics. Generally these allow water to pass fairly freely, and consequently any article fabricated from sheet material so processed is liable to leak badly at the seams. It has been found entirely satisfactory to paint or dress such seams with a synthetic resin. Bedafin 385 or 585 dissolved in suitable organic solvents gives on evaporation of the solvent, flexible water resistant coatings, which effectively seal the sewings and which adhere tenaciously to the bitumen, wax or oil-treated fabric. Seam proofing is essential in gas or airtight fabrics as in many

water-proofed goods and this method is simple and economical in application and effective in performance.

Synthetic resins have played a large part in meeting several problems connected with war-time finishing. Many of these are unfortunately, of such a nature that their discussion here is not permissible. Of those uses to which I may refer the following will probably be of most interest. Shelter life has produced its own problems, chiefly as a result of the humid conditions obtaining in many shelters in wet weather. Canvas bunk fabrics would probably be finished normally with starch and might in many cases be quite satisfactory provided that an antiseptic to prevent mildew growth was added to the finishing mix. However, one specification has been issued which calls for the application of a wash-fast mildew resistant finish coupled with some filling and stiffening of the fabric. By the treatment of the woven cloth with an aqueous solution of a synthetic resin (Bedafin 2001) suitably heat-processed to render it fast to washing, a material possessing the required properties has been provided. Such a fabric is more resistant to dampness, is easily cleaned by sponging with water or an antiseptic solution and possesses the desired rigidity and strength.

Fortunately, however, we do not spend the majority of our time in shelters. During the period we are above ground after black-out, all lighted windows must be obscured to the maximum extent. In the early days of the war some amusing make-shift devices were to be seen for achieving the necessary darkening of windows. Most of these were very short-lived and the demand for more effective and attractive black-out fabrics arose. The Institute has supported the issue of a specification covering the testing and evaluation of materials marketed for black-out purposes. Several excellent fabrics, gaily patterned on one side at any rate, but with the essential opacity have been marketed. For heavier and more severe duty, synthetic resin processed cloths have been prepared. Where large factory or laboratory windows have to be protected it is obvious that a more robust material is required than the domestic market demands. Intensity of lighting is often higher and the usage is liable to be rougher, consequently ordinary starch fillings or similar processes do not give cloths possessing satisfactory mechanical properties.

To be completely satisfactory a black-out cloth must combine opacity with flexibility, must be non-flaking and non-cracking, should not dust and at the same time it should be spongeable. Such a finish offers obvious problems particularly if the base cloth which is used is of a light nature and demands the application of large amounts of pigments in order to obtain satisfactory opacity. By utilising the thermo-plastic resins which in many cases possess excellent binding power for pigments, and by giving body both to the finish and to the finishing mix by the addition of a water-soluble cellulose ether derivative, a very satisfactory cloth is produced.

As an example, a recipe calling for the use of the following quantities of materials has given entirely satisfactory effects under works conditions —

- 25 lbs of China Clay are boiled with
  - 2 gallons of water, until deflocculated and to this is added with thorough stirring
- 25 lbs Bedafin D (an aqueous dispersion of a thermoplastic resin)
- 58 lbs of a Carbon Black Paste are then mixed with
- 50 lbs of Bedafin D and the two liquors are thoroughly mixed
- 2½ lbs Cellofas WFZ are dissolved in water, and to this is added a further
- 50 lbs Bedafin D which in this case is added a little at a time and well worked in. Into this mix the Carbon Black, China Clay-Bedafin D mixture is worked, and finally
- 25 lbs Dibutyl phthalate or tricresylphosphate are mixed in and the whole liquor is stirred thoroughly until it is uniform

Approximately 250 lbs of filling mixture is prepared in this way, which is sufficient for covering about 300 yards of a 3-4 oz. cloth. The mixture is of a sufficient consistency to be applied on a spreading machine to both surfaces of the cloth, drying in between each application at a temperature of not less than 60° C.

Another useful application of synthetic resins of the same type is bonding fabrics for certain war-time purposes. A mix of a water-soluble cellulose ether and a thermoplastic resin is prepared and where spreading machinery is available the mix can be produced with a sufficiently high viscosity to allow it to be spread, but if only back-filling machines are available, then by the addition of more water the viscosity can be reduced to admit its application by this means. The bonded fabrics available for inspection, have been produced by the use of a mixture containing 2 parts of Cellofas WLD added to 100 parts of Bedafin D. Plasticisers may be incorporated where it is desirable to produce a more flexible effect.

Leaving the question of synthetic resins for application to textile fabrics, by orthodox methods another outstanding use has been made of these products during war-time. Probably the greatest inconvenience caused by modern aerial warfare from the point of view of the civil population is the damage caused to glass windows. These are often shattered even though they are located in buildings relatively distant from the spot where an actual "incident" has taken place. For this reason and because modern machinery would soon suffer irreparable damage if exposed to the weather in factories from which windows had vanished, there has arisen a real demand for what are termed "window replacement fabrics". A window replacement fabric may be prepared by a variety of methods.

(1) Viscose film or cellulose acetate film may be bonded to one or both sides of a cotton net by means of a synthetic resin, (2) a cotton net or wire mesh fabric may be completely filled with a continuous film of a suitable synthetic resin, (3) an ordinary fabric (cambric) as opposed to a net may be impregnated with a resin or oil dope in order to give it a weather-proof translucent finish. All these methods, however, call for the use of very substantial quantities of the synthetic resin and an improved method of producing the desired effect has been devised whereby considerable economy in the amount of synthetic resin consumed is effected.

Before considering in detail the methods for producing these fabrics a few remarks upon the desirable properties of the resins used may not be out of place. Obviously the resin must give a transparent film possessing good mechanical properties including flexibility and strength and also the film must be resistant to destruction on exposure to weather. This latter property is of paramount importance and in examining resins for this purpose the effect of wind, rain, sun and frost must all be taken into account. In addition the film must possess the property of wearing clean—that is dirt falling upon the fabric must be easily removed either by subsequent rain or by washing with water. Many of the window replacement fabrics marketed have suffered very badly from the defect of soiling in such a way that subsequent cleaning was by no means an easy matter.

One of the most satisfactory resins for the production of window replacement fabrics of any of the types above mentioned is Bedafin 2001, which meets all these requirements. Broadly speaking the method of preparing a transparent window replacement fabric of the filled cotton or wire net type as opposed to the production of translucent resin coated cambrics, is as follows. The net should first be stiffened with starch, glue, or by the application of a small amount of the synthetic resin, so setting the structure of the net and preventing subsequent distortion during processing. The net

should then be drawn through the resin solution and dried preferably by passage up a heated vertical tower similar in principle to that used in the manufacture of oiled silk fabrics. The thickness of the film on the netting is controlled by the rate of travel and the viscosity of the solution used, and finally the resin when dried, should be polymerised by means of a short heat treatment in order to render it water and weather resistant.

Generally about 30 lbs of solid resin are required per 100 sq yards of net, this calculation being based on the assumption that the net is about 10 mesh and weighs 10-11 lb per 100 sq yards.

The more economical method of producing window replacement fabrics of this type involves a three-stage process. The net is first water-proofed with a wax/aluminium salt proofing agent in a single-bath process and is then dried. The purpose of this treatment is to prevent the cotton yarns from drawing moisture into the fabric by capillary attraction when the material is cut for use and the ends of the cotton threads become exposed to the weather.

The water-proofed net is then filled with a suitably softened starch solution and is again dried. For this purpose about 3½ lbs starch in 10 gallons of water with an addition of 2 ozs Calsolene Oil HS or 4 ozs ordinary Turkey Red Oil 50 per cent Soda Finish is satisfactory. The net is completely filled by passage through this boiled starch liquor, the excess being removed by doctors or by any other suitable means. Care should be taken, however, to apply sufficient of the starch paste to fill the net structure completely. It is generally found advisable to carry out the filling operation using the starch at a temperature of about 105-120° F (40-50° C) and when filled, the net is dried and passed forward for resin coating. The third and final stage of the processing involves padding the starch filled net through a synthetic resin dope in order to give a protective coating to the starch filling and so preserve it from the ill effects of the weather. It is advisable to apply a highly plasticised mix containing Bedafin 2001 from a solution in suitable organic solvents. Generally using a 50 per cent solution of the resins and securing about 200 per cent take-up entirely satisfactory results are obtained provided that as in the case of netting completely filled with resin, the film is finally polymerised by a short heat treatment after drying.

By this means the consumption of synthetic resin is reduced from about 30 lbs solid resin per 100 sq yards to approximately 6 or 7 lbs. This is not only important in view of the need for the conservation of all supplies of resin, but it results in a substantial reduction in production costs and simplifies working in some respects.

In place of starch, cellulose ethers, alginates and similar film forming substances can be used to fill the net and provide an inert support for the final resin coating.

Cambric fabrics can be rendered translucent by simple padding through the neat Bedafin 2001 plasticised in a satisfactory manner. The material may require double padding in order to secure the presence of sufficient resin. Once the necessary amount of resin has been applied to the fabric and polymerised by heat treatment, a fabric possessing high resistance to weathering and of good translucency is produced. These fabrics, of which examples are available for inspection, have been widely adopted both for domestic and industrial use. They possess advantages over the viscose or acetate film type fabrics in that they are much more resistant to weather, do not tend to separate into an unsupported film of relatively poor mechanical strength and a cotton net which alone provides no protection against weather, nor are they subject to the variation in dimensions so frequently encountered when the bonded film type fabric meets variable weather conditions.

Before leaving the uses of synthetic resins in connection with war-time finishing, there is one more interesting use which I should like to mention.

With the extension of the zone of military activity to the Eastern theatre of war, a demand for mosquito and sand-fly netting has arisen. This netting it is obvious, will be used under extremely severe conditions and any finish applied to it should be durable and not liable to bacterial or mildew attack. Also, if long life is to be secured, the finish should impart added mechanical strength to the net without greatly increasing the weight. A finish based on the use of sufficient starch to give the necessary rigidity has been evolved, but this, in my opinion, is likely to be of only mediocre value in actual use. If accidentally wetted the nets will lose rigidity and the mesh will collapse, for under present conditions warp knitted fabrics are being used to supplement the supply of true net. Where starch is used, an adequate addition of Shirilan should certainly be made to give protection against mildew attack, a damage very liable to occur under conditions of use which these nets will encounter. It is much preferable to apply a synthetic resin finish which is relatively immune from attack by mildew and bacteria, and which will confer strength and rigidity to the net and withstands wetting or even washing. A thermo hardening resin of the Bedafin 2001 type applied from an aqueous dispersion would meet these conditions admirably.

Amongst other problems related to war-time processes there are one or two which may be of passing interest. The question of rot-proofing has received considerable attention, but judging by the number of wholly or partially rotted sandbags to be seen daily, it appears that much remains to be achieved in this field. This is all the more remarkable when one considers the very cheap but simple and highly efficient methods available for producing fabrics highly resistant to bacterial attack. The use of metallic naphthenates which require to be applied from organic solvents, with consequent fire hazard, and expense, have been followed by the introduction of aqueous dispersions of suitable metallic naphthenates which possess good rot-proofing properties.

An even simpler and cheaper method depends upon the deposition on the fabric of a sufficient quantity of basic copper carbonate. Basic copper carbonate dispersions under the title Burgundy or Bordeaux mixtures are used as horticultural sprays. Their application to textiles does not, however, appear to have previously been tried. The carbonate may be applied either by a double-bath process in which the cloth is first impregnated with the copper sulphate solution and is then subsequently passed through a cold soda ash liquor forming the basic copper carbonate in situ or alternatively a single-bath process may be used in which the cloth is treated in a prepared dispersion of copper carbonate in water. The choice of methods to be adopted will depend to some extent upon the nature of the fabric involved. For sandbags and light-weight cotton fabrics generally, the single-bath method is entirely satisfactory, but for heavy cotton duck cloth of the type frequently specified for service use, the two-bath method is preferred as this gives superior penetration.

Rot-proofing sandbags and similar goods by the one-bath method is extremely simple. The following formula may be of interest —

- 10 lbs. of Copper sulphate crystals (preferably crushed small) are dissolved in a wooden vessel of about 50 gallons capacity, and the liquor is made up to 30 gallons with water
- 11½ lbs of Soda Crystals or
- 4 lbs of Soda Ash are dissolved in
- 4 galls of Water at about 50° C. The solution is allowed to cool and when cold is poured into the copper sulphate solution, stirring thoroughly in order to ensure good mixing. In order to obtain as fine a dispersion as possible about
- 2 ozs Calsolene Oil HS are now added to the mixture and it is made up to 40 gallons by addition of cold water

The percentage concentration of basic copper carbonate in the mixture is approximately  $2\frac{1}{2}$  per cent. The goods are immersed in this liquor until thoroughly saturated, and are then squeezed so that they pick up their own weight of solution, are lightly rinsed in cold water and dried. This same mixture may be used for treating goods continuously on the padding machine if the cloth is not too tightly woven. When cotton goods are being processed the padding liquor can be used at  $40-50^{\circ}\text{C}$ .

In order to avoid leaving free alkali in the cloth, a condition which sometimes results in a weakening and loss of strength of jute material on long exposure, the amount of soda ash used is slightly less than that necessary completely to precipitate all the copper sulphate. Calsolene Oil HS is used as a dispersing agent to improve the fineness of dispersion, but it should be noted that the quantity of Calsolene Oil HS or other wetting agents used should not be increased by any very great extent over that recommended since, if the wetting agent is retained by the fabric, there is a risk of the copper carbonate being leached out of the cloth on long exposure to water. The prepared mixture is reasonably stable, but should be applied for preference within 24 hours of making up, since the rot-proofing efficiency of the liquor is found to decrease if the liquor is left standing for several days before use.

In applying the two-bath process the goods are first impregnated in a 2 per cent solution of Copper Sulphate Crystals which may be applied at any temperature up to the boil, squeezed to 100 per cent expression and then passed through a cold 5 per cent solution of soda ash. The goods are subsequently squeezed to remove excessive liquor, are rinsed in cold water to remove free alkali, and are finally dried at a temperature not exceeding  $60^{\circ}\text{C}$ . An addition of 1 oz. of Calsolene Oil HS or other suitable wetting agent to every 40 gallons of Copper Sulphate Solution is recommended in order to obtain good penetration and, of course, metal vessels should be avoided when using the Copper Sulphate solution, in view of the known effect of this liquor on metals.

Both these methods give a very satisfactory measure of protection against rotting. Some idea of the extent of this protection can be judged by tests carried out on jute and cotton fabrics treated by both processes. These test patterns were buried in good garden soil under approximately similar conditions for a period of 4 months. Control patterns of untreated jute fabric buried at the same time had disappeared completely at the end of 4 months, the cotton controls being almost entirely destroyed, but patterns treated by both the methods described showed only slight visible deterioration, the fabrics after this very severe test being still in a thoroughly serviceable condition. The cost of the process is very low. It is found as a rule that it works out at approximately 0.1d per sandbag. This cost should be considered in relation both to the value of the bag and to the 5-fold increase of life which it is conservatively estimated the process confers upon the fabric.

The rot-proofing method outlined if followed by a Waxol W or other single-bath proofing process permits various service requirements to be easily and cheaply met. Camouflage netting and duck cloth is very readily processed by this means without any fire risk such as is entailed by the use of metallic compounds dissolved in organic solvents. The convenience and comparative cheapness of the process will probably bring to light many new uses for rot-proof fabrics when the present war is over.

To turn now from the fabrics directly related to the war effort, there is an equally large and varied range of problems on the civilian side. Supplies of raw fibres having been severely reduced, it is the duty of both processor and user to endeavour to prolong the useful life of all garments and furnishings to the fullest extent possible. Considerable success in improving the

abrasion resistance and the useful life of sheetings, overall cloths and the like has resulted from the application to these fabrics of alkali soluble cellulose ethers or certain selected synthetic resins. Generally the application of 5 per cent alkali soluble cellulose ether of the Cellofas AF type increases the wear-resistance of the cloth very substantially. A similar improvement in resistance to wear can be obtained by the application of thermoplastic resins such as Bedafin D, and permanent sheetings and durably finished overall cloths produced in this manner present considerable advantages over the normally finished cloths.

A widely used filling agent and finishing assistant commonly encountered in all branches of the textile trade is, of course, starch, in one or other of its many forms. It has been found that in the laundry trade very substantial economies in the use of this product can be effected by the introduction into the starch liquors of a small amount of certain selected wetting and dispersing agents. The mechanism of the action is by no means well understood, but it is a fact that if 1 per cent of an alkylated naphthalene sulphonic acid derivative such as Perminal WA be added to a starch liquor, the addition being calculated upon the weight of dry starch used in the laundry operation, no difference in finish is detected and the amount of starch is reduced by approximately 30 per cent. This feature will not, of course, interest those who desire to size or starch-fill to weight, since obviously if the amount of starch applied to a fabric is reduced, then the added weight is similarly reduced.

Similarly synthetic resins have been applied along with starch in back-filling operations and in other finishing processes. Bedafin D previously mentioned, or Bedafin A (a synthetic resin soluble in weakly alkaline liquors), have both been satisfactorily employed for this purpose. By varying the proportions of resin and starch in a finishing mixture it is possible to reduce substantially the consumption of starch and yet by avoiding the use of the resin alone, keep the cost of the finish within reasonable limits.

The substitution of cellulosic fibres for wool in the production of suitings and "worsted flannel type" cloths, has enabled the finisher to display his art to perfection. Some of these fabrics in which the wool has been wholly replaced by cellulosic fibres possess insufficient rigidity and are lacking in fullness. Such cloths lend themselves admirably to finishing processes in which synthetic resins are employed. Mixtures of Bedafin 2001 with Bedafin 785 or 285X as a plasticiser, and applied from an aqueous ammoniacal liquor, give full woolly finishes. Alternatively by the use of Bedafin D or Bedafin A along with a fatty alcohol softening agent the desirable fullness of handle and necessary draping properties can be secured. Though such finishes may look like wool and handle like wool, yet they will lack one important property which makes wool such a satisfactory fibre for outer wear fabrics. This is the property of resisting wetting, and therefore on such cellulosic cloths a water repellent finish should certainly be applied.

If a fabric is to be produced which will "wear clean" then wax proofing agents should not be used for it is well known that wax-containing proofing agents tend to collect dirt. Thus purchasers who, with the advent of rationing by the coupon system will require their clothes to last as long as possible, will be better satisfied if the whole of the finish—softening, filling and proofing—is carried out by the use of durable products which will tend to enhance the wearing properties of the garments. It is unnecessary to render these goods fully water repellent, but if they are given the repellency inherently possessed by wool, then the consumer's demands are met. Mechanical finishing plays a prominent part in producing wool like fabrics and in this respect conditions both of tension and temperature in drying require close attention. A "Sanforising" or decatizing process in the final stages of finishing is often of considerable aid in securing the "cloth" handle and appearance which is so desirable.

The hosiery trade, too, has suffered a severe restriction in the prohibition of silk hose. The wearers of silk hose take badly to their present substitutes, Lisle hose, which, in many respects, do not possess the desirable properties of all-silk hose. However, it is the duty of all finishers of hose to make as attractive as possible the Lisle and rayon hose which are now universally worn. Very attractive finishes can be imparted to these goods by careful application of small quantities of selected synthetic resins. Springiness and improved appearance result from the application of quantities as low as 0.5 per cent of Bedafin D, either alone or in conjunction with a sulphated fatty alcohol softener. Although the finish is not wholly permanent yet it possesses sufficient durability to enable the hose to be worn and washed without losing the finish. Where a softened finish is desired, then the application of a trace of Velan PF provides a satisfactory effect, and if the hose are dried on forms at the temperatures which can be attained in most hosiery plants, then the finish will process resistance to washing and should, at any rate, last the life of the hose.

Whilst real silk has been replaced by Lisle and rayon in the hosiery trade, a similar substitution has taken place in the linen industry and Ramie is now becoming more widely used in this section of the trade.

One of the difficulties associated with Ramie is that of securing adequate fibre control during spinning and of getting a softened yarn with good laying of the surface fibres. These points are valued by spinners of Ramie and it assists in producing such effects if, prior to spinning, the Ramie fibre is lubricated with solution of a sulphated fatty alcohol softening agent. Very promising effects have been secured by the use of 3 lbs Cirrasol SA dissolved in 10 gallons of water, or by the use of a similar solution of Calsolene Oil HS. Sisal, an Empire produced fibre, has also been the subject of considerable attention in view of its availability, and although so far this material has not entered the textile trade in any quantity, except for the manufacture of twines, cords and the like, with improved knowledge of its properties and a full recognition of its potentialities, this fibre may in the future provide us with yet another useful raw material.

Finally, there have been problems concerned with actual recovery for re-use of materials, which under normal circumstances, would have been discarded. In normal times salvage of some materials may not be an economic success, since the margin between the cost of recovery and the cost of replacement may not be sufficiently great. In war-time, however, salvage is of paramount importance and, of course, the margin between the two costs is of much less importance. An interesting case arose recently when the question of recovering the heavy-weight high quality wool fabric used as air filters in certain factories was discussed. Some of the dust-collecting bags are heavily loaded with magnesium powder and if this can be satisfactorily removed then the bags can be re-used. A process was devised whereby on treatment in dilute acid, the metals are dissolved and subsequent washing with fatty alcohol sulphate detergents in acidic liquor clears the bags and leaves them in a condition fit for further service. Similarly, the wool blankets from sanforising machines which become heavily loaded with starch and finishing agents can be reconditioned and the consumption of much valuable wool thereby be materially reduced.

In conclusion, these notes may appear to you somewhat disjointed, but they do, I hope, convey to you the wide variety of problems which the finishing trade as a whole has been called upon to attack during the course of the past 18 months under abnormal conditions.

I thank you for your attention and for the invitation to speak to you, and I also have to thank I C I (Dyestuffs) Ltd for permission to present this paper.



## Lancashire Section

On May 29th the Lancashire Section held a meeting under the Chairmanship of Mr B Hesketh, at which Mr F Chadwick, Mr E Leigh and Mr Ashton opened a discussion on " Raw Materials for Lancashire Textile Production in War-time " The points raised covered a wide field and included a suggestion for a standardised multi-purpose domestic cloth made from those qualities of cotton and counts of yarn which would be least in conflict with the requirements of the State for war purposes

It was generally concluded, however, that there was no available source of raw material remaining untapped and that in both waste and virgin fibre what material was available was already being used to the best advantage

# THE JOURNAL OF THE TEXTILE INSTITUTE

Vol XXXII

AUGUST 1941

No. 8

## PROCEEDINGS

### NOTES AND ANNOUNCEMENTS

#### Textile Institute Competition Awards, 1941

#### COMPETITIONS FOR WOVEN FABRICS, KNITTED FABRICS, YARNS AND DESIGNS FOR PRINTED FABRICS

In 1941 it was found possible to hold all except "A" Competition in the annual competitions organised by the Textile Institute with the object of encouraging the advancement of structure and design in textile fabrics. The numbers of entries to the various sections were very gratifying in view of the difficult conditions under which students have had to work during the past year. The Competitions are open to British students throughout Great Britain and Northern Ireland.

Prizes for these competitions are provided from the Crompton Memorial Fund, the Beanland Bequest and other donations which have been provided for this purpose.

The following prizes have been awarded and arrangements for the distribution of prizes will be published in due course.

#### (B) Competition: Yarns

##### Class I. Novel Folded Yarns

First Prize (£5)	.. Frank Derek Jagger (Bradford Technical College)
Second Prize (£3)	... Maxwell S Canavan (Bradford Technical College)

##### Class II: Novel Single Yarns

First Prize (£3)	. Fred Anderson (Bradford Technical College)
Second Prize (£2)	. Maxwell S Canavan (Bradford Technical College)

#### (C) Competition: Special Woven Fabric

First Prize (£5)	Michael Naylor Holmes (Leeds University)
Second Prize (£4)	. Kenneth Haley (Dewsbury Municipal Technical College)
Third Prize (£3) ..	John Fielding (Dewsbury Municipal Technical College)
Fourth Prize (£2) ..	... Ronald Preece Goddard (Huddersfield Technical College)

**(D) Competition: Special Woven Fabric (City and Guilds)**

First Prize (£3)	John Maude (Huddersfield Technical College)
Equal Second Prize (£2)	John Emmott Atkinson (Burnley Municipal College)
Equal Second Prize (£2)	Ronald Virgo Nixon (Bradford Technical College)
Prizes of £1 each	Arthur Crossley (Bradford Technical College)
	Stanley Lister Dewhurst (Keighley Technical College)
	John Richard Horsley Gregson (Bradford Technical College)
	John Eastwood Hartley (Burnley Municipal College)
	William Wood Kenyon (Huddersfield Technical College)
	Irvin Roberts (Bolton Municipal Technical College)

**(E) Competition: Knitted Fabric**

First Prize (£5)	Donald Wilford Sherriff (Leicester College of Technology & Commerce)
Second Prize (£3)	Ronald Percy Johnson (Leicester College of Technology & Commerce)
Third Prize (£2)	Norman Cartwright (Leicester College of Technology & Commerce)
Prizes of £1	Donald Joseph Burton (Leicester College of Technology & Commerce)
	Roger Duffey (Leicester College of Technology & Commerce)

**(F) Competition: Designs for Printed Fabrics***Class I* Designs for Dress Materials

First Prize (£6)	Elsie Beardow (Manchester Municipal School of Art)
Second Prize (£4)	Clifford Metcalfe (Manchester Municipal School of Art)
Third Prize (£2 10s od)	Joan Davison (Manchester Municipal School of Art)

*Class II: Design for Furnishing Fabric*

First Prize (£5)	Marion Helliwell (Bradford Tech College)
Second Prize (£4)	Donald Bentley (Bradford Tech College)
Third Prize (£2 10s od)	Kathleen Lomas (Manchester Municipal School of Art)

**(G) Competition: Special Woven Fabric (Worsted)***Class I* Men's Wear

First Prize (£3)	James Henry Berry (Bradford Technical College)
Second Prize (£2)	John Richard Horsley Gregson (Bradford Technical College)
Third Prize (£1)	Norman Hodgson (Halifax Municipal Technical College)

*Class II* Women's Wear

First Prize (£3)	James Alexander (Bradford Technical College)
Second Prize (£2)	James Henry Berry (Bradford Technical College)

**(H) Competition: Woven Fabric (Worsted)—(City and Guilds)**

First Prize (£3)	Ronald Preece Goddard (Huddersfield Technical College)
Second Prize (£2)	James Henry Berry (Bradford Technical College)
Prizes of £1 each	Stanley Lister Dewhurst (Keighley Technical College)
	William Wood Kenyon (Huddersfield Technical College)
	Leslie Teale Sowden (Bradford Technical College)

**ROYAL SOCIETY OF ARTS****Result of Competition for Students of Textile Design, 1941**

The following are the winners of the two scholarships' of £100 each offered by the Royal Society of Arts for students of textile design —

**Furnishing Textiles**

Miss Lorna M C Pillow (student of the Royal College of Art)

**Dress Textiles**

Mr Kenneth O'Brien (student of Hull College of Art & Crafts)

Awards were also made for the best individual design submitted in either group of the Competition, Miss Lorna M C Pillow (student of the Royal College of Art) and Miss Mary W Duncan (student of Edinburgh College of Art) were bracketed for first place —

THE SIR FRANK WARNER MEMORIAL MEDAL Miss Pillow

NORTH LONDON EXHIBITION TRUST

(A prize of books to the value of £5) Miss Duncan

\* The Scholarships will be for the purpose of helping to maintain students in London or other centres for at least one year while attending the Royal College of Art or some other approved Institution, or while gaining technical or other experience in an approved factory, studio or retail establishment, or for part-time instruction in a school and part in another establishment

**NOTICES: INSTITUTE MEETINGS**

Tuesday	2nd September	1 30 p m	Meeting of the Publications Committee at the Institute
Tuesday	2nd September	2 45 p m	Meeting of the Diplomas Committee at the Institute
Wednesday	17th September	1 30 p m	Meeting of the Finance and General Purposes Committee at the Institute
Wednesday	17th September	2 45 p m	Meeting of the Council at the Institute
Friday	19th September	2 45 p m	Meeting of Committee on Recruitment, Selection and Training for the Textile Industry, at the Institute

**CORRECTION**

In the July 1941 *Journal*, P70, 14th line from the bottom should read "watched the final water-repellency should meet the tests usually encountered."

## WOOL—THE WARP AND WOOF OF THE BRITISH COMMONWEALTH OF NATIONS \*

By A FOSTER DU PLESSIE, M A

(Chairman of the International Wool Publicity and Research Secretariat)

In talking of wool no more fitting description of it can be given than to call it the Warp and Woof of the British Commonwealth of Nations. Like the warp threads running the length of the fabric, wool runs through the history of the Empire. Like the weft threads interweaving the whole structure of the fabric, the great economic importance of wool does the same to-day to the British Commonwealth of Nations.

The sheep as a domestic animal goes back to very early times, and that wool was used by earliest civilised man is shown by records in the Bible and in Greek mythology. The Golden Fleece of Jason's Quest was no doubt symbolic of the value placed by the Greeks on wool for the finest clothing. Some of the forms in which wool clothing was used hundreds or even thousands of years ago may still be seen to-day. The Arab amidst the desert sands still wears a burnous of wool to protect him from the burning sun by day and from the rapid change of temperature to the bitter cold of desert night, just as did his ancestors in Biblical times.

When the Romans landed in Britain in 55 B.C., they found the early Britons with flocks of sheep and a developed wool industry. The Romans acquired and developed their knowledge of spinning and dyeing wool, and it was from the new established centres in Britain that "wool so fine it was comparable to a spider's web" was sent to the Roman Emperors. The Saxon invasions led to the destruction of the Roman wool industry, but, following the Norman Conquest, there was a great development of sheep breeding, and by the twelfth century important wool manufacturing centres were established in the West of England, at Bristol and Exeter. In 1111, Henry I established the Scottish industry at the mouth of the Tweed.

Up to the fourteenth century most of England's raw wool, however, was still exported to the Continent for processing and dyeing, but under Edward III the first transfer of Flemish workers to Britain, accompanied by the prohibition of exports of raw wool and imports of cloth, made Britain both the chief wool-growing and manufacturing country of Europe. In 1454 Parliament declared that the "making of cloth within all parts of the realm is the greatest occupation and living of the poor commons of this land."

Under the reign of Elizabeth 80 per cent of exports consisted of woollen goods, and further measures were taken to increase the use of wool. Everyone over the age of seven had to wear a wool cap when out of doors on pain of fines of three shillings and fourpence for each offence.

Up to the middle of the eighteenth century the wool manufacturing industry was mainly a domestic one, but the discoveries of Hargreaves, Kay, Arkwright and Crompton made mechanical spinning and the development of large-scale industry possible. England's domestic wool production became insufficient for her needs. At the end of the eighteenth century wool began to be imported from Spain, and at the beginning of the nineteenth century from Germany.

In the nineteenth century the great wool manufacturing industry of the West Riding of Yorkshire reached its full development, while the Scottish and the West of England industries became noted for specialised types of production. More and more wool was required, and in the nineteenth century Britain began to draw her wool from the Dominions—Australia, South Africa, and New Zealand—which to-day produce the bulk of the world's wool.

---

\* Lecture given to the Royal Society of Arts, London, on 22nd April, 1941.

**Development of Wool Production in the Dominions,**

I think it is worth while to devote a little time to the spectacular rise of the sheep-breeding industry in these Dominions

The start of the South African sheep industry dates from the time when the King of Spain presented the Dutch Government with two merino rams and four ewes, and these were sent to Colonel Gordon, the commandant of the Dutch East India Company at the Cape. After the Napoleonic Wars more merino sheep were imported from Saxony, to which country the Spanish Escorial merinos had been imported at the end of the eighteenth century. Sheep were largely responsible for the subsequent territorial expansion of the Colony. By 1888 Cape Colony had 10½ million sheep, the Orange Free State 6 million, and large flocks were also found in the Transvaal and Natal.

Following the Union of South Africa in 1910, vigorous measures were taken to control disease and improve the quality of both sheep and wool. Research work done at Onderstepoort, and extension work by the Department of Agriculture has done much to achieve this.

Sheep numbers rose steadily until in 1930 the record number of 44 million sheep was reached. Then came the double disaster of renewed depression and one of the worst droughts which ever afflicted South Africa. Millions of sheep died, and by 1935 the sheep population had once more fallen to 30 million. Undaunted, however, South Africa has returned to the task of building up her flocks, and to-day merinos once more total 35 million, and improvement in wool quality has proceeded perhaps more rapidly in the last ten years than ever before.

The foundation of the great Australian sheep industry was laid by Captain John MacArthur, who in 1797 bought three rams and five ewes from a selection brought by Captain Waterhouse from Colonel Gordon's merino stud at Cape Town. In 1804 MacArthur took the first of his wool to London, and encouraged by opinions of it, he returned with the fixed resolve to grow in Australia merino wool as fine in quality as any produced in Spain. In Australia sheep found virgin pastures untrodden by other ruminants, and therefore untroubled by the terrible animal diseases with which Dutch and British settlers had to contend in South Africa. From a few thousand sheep in 1820 numbers increased to 60 million in 1880 and 107 million in 1890. In 1890 began a drought more widespread and terrible than had ever been experienced before or since. By 1903 sheep numbers had fallen by over 50 million. Yet, despite these setbacks, numbers have climbed up once more to the new record of 116 million. Besides, the average weight of fleece has increased during the last fifty years from 5 lb. to 9 lb. per head, thus almost doubling wool production over that period.

New Zealand started to breed merinos soon after the foundation of the Colony in 1890. The discovery of how to freeze meat and transport it in cold storage caused a rapid change in New Zealand sheep industry. The rich pastures of New Zealand are ideally suited to the production of the finest lamb, and this could now be sent to Britain. Hence, cross breeding was embarked upon with the object of producing a quick fattening lamb as well as good commercial wool. As a result of experiments in the inbreeding of the progeny of the Lincoln/Merino cross, the Corriedale breed, which is a dual purpose animal, was evolved. New Zealand sheep numbers have increased steadily and now amount to 31 million.

The three Dominions produce over 70 per cent of the clothing wool and over 90 per cent of all Merino wool which enters into the international trade of the world. Next in importance to the Dominions as wool producers are the South American countries and the United States.

### **The Economic Importance of the Wool Industry to the Empire**

The economic importance of these vast Dominion wool industries to the British Commonwealth of Nations need hardly be emphasised. The aggregate value of Australian wool production over the last decade varied from £A50-60 million, thus equalling nearly half of Australia's income from all exports. In 1940, value reached the record of over £A65 million. South African wool is valued from £10-13 million, and is by far the greatest primary product. The value of the New Zealand wool clip varies from £NZ12-20 million annually, the value of exports ranking next in importance to butter, mutton and lamb.

Before the war the British wool textile industry consumed between 30-40 per cent of Australia's wool, nearly 60 per cent of New Zealand's wool, and about 20 per cent. of South Africa's wool.

Goods exported by the British wool textile industry amounted to an average annual value of nearly £40 million. About a third of this total was exported to Commonwealth countries. Total imports of the three wool-growing Dominions from Britain amounted to nearly £100 million, i.e. not much less than a quarter of the total value of United Kingdom exports.

I think these figures may give some idea of the importance of wool as the "woof" of the British Commonwealth of Nations—of the direct link between Dominions wool growers and the British wool industry, and the indirect but no less real link between prosperity caused by the wool industry in these Dominions and all sections of British industrial life.

In view of the tremendous importance of wool to the economy of the Dominions in particular, as well as the Commonwealth as a whole, there is much need to keep a close watch on every change in the trend of production and consumption.

Unfortunately, in the interval between the last war and the present one, this trend, considered in its widest sense, has not been devoid of unfavourable aspects. True, the further rapid increase in the quantity of wool produced in each of the main sheep-raising countries has contributed to enrich the world.

In Australia, average annual wool production in the period 1934-5/1938-9 was 45 per cent higher than in the period 1914-18. In South Africa the increase over the period dividing the two wars was 41 per cent, and in New Zealand 29 per cent. Total world production increased by over a third (35 per cent.)

This increase in production has been due partly to the increase in sheep numbers and partly to the increase in the average yield per sheep.

It took place in a world which had not yet recovered from the economic repercussions of the last war, and which did much to enhance these difficulties by building up new barriers of tariffs and other trade and exchange restrictions. While, throughout the nineteenth century and right up to 1913, the rapid growth in population and the expansion of the wool manufacturing industry caused the trend of wool consumption to rise still more rapidly than production, this relationship of consumption to production was exactly reversed in the years following the last war.

Up to the outbreak of the present war the most important wool-consuming countries in the world were the United Kingdom, U.S.A., France, Germany, Italy, Belgium and Japan.

An analysis of the trend of wool consumption in the seven most important consuming countries over the war-dividing "peace" period reveals that consumption did increase for the group as a whole, but much less rapidly than world production of wool.

The wool-growing industry is individualistic and conservative in its ways. There was little natural inclination among woolgrowers to "manage" their commodity. "Sell and repent, but sell" has always been their slogan, and the structure of a free world market open to all, based on the auction system,

supported this policy. Even during the difficult years following the last war, carryovers from one wool season to the next were small, but such realisation of the world's wool clip could only be maintained by sacrificing prices. With the exception of two or three peaks, wool prices have been on an unprofitable basis throughout the decade preceding the outbreak of the present war.

Gradually Dominion wool producers came to realise the need for co-operation. In January, 1937, there met in Melbourne representatives of the wool growers of South Africa, Australia and New Zealand, in order to determine how jointly they might best promote the interests of the wool industry. Before this they had induced their respective Governments to impose a statutory levy on all wool exported, in order to derive funds to serve this purpose, these funds amounted to over £A70,000 in Australia, £NZ18,000 in New Zealand, and £40,000 in South Africa, or together, over £100,000.

As a result of that Conference, it was decided to establish a permanent Secretariat, to be known as the International Wool Publicity and Research Secretariat, which would have at its disposal the sum of £50,000 annually, to which, pro rata to the volume of their wool exports, the three Dominions would contribute. In addition, it was agreed that from their separate funds the contributing bodies should, in their respective countries, promote wool consumption and subsidise and assist such biological and other scientific research as would conduce to the highest productive efficiency of wool.

Comprehensively the aims of the I W S, which was established in London in 1937, may be defined as the furtherance of the interests of the wool industry in its widest sense. Not the promotion of Australian, New Zealand and South African interests separately or collectively, but the interests of wool growers no less than those of wool manufacturers throughout the world, since the three Dominions have realised that the interests of all sections of the wool industry are indissoluble.

The methods by which it was hoped to further these objectives may be grouped as follows —

- (1) Scientific and economic research.
- (2) Promotion and Publicity.
- (3) International Co-operation.

A careful investigation of the industry in all its phases determined the policy and programme of the I.W.S. But the completion of this fundamental economic research did not, of course, terminate its interest in economics, for it is obviously essential for the I W S to continue to be extremely well informed on all developments in the wool industry as well as in related industries.

Scientific research forms a major plan in the programme. This includes fundamental and long-range researches into the composition of the wool fibre, technical work on behaviour in processing with a view to opening up new uses, and physiological investigations on health and hygiene of wool clothing. Approximately one quarter of the total financial resources is devoted to scientific research.

When the vast appropriations of many individual industrial and commercial firms for publicity are considered, it will be realised that the revenue of the I W S is extremely small for covering the world by means of promotion and publicity. One result of this has been twofold. It has stimulated quality and style consciousness in production and it has increased consumer acceptability and demand in consequence.

Time does not permit of any discussion on the media employed, which range from educational material made available to schools, lectures to sales staffs of retailers, exhibitions, films, fashion shows, radio, television and the press. Naturally the fact that an international commodity and not a proprietary



brand of merchandise was being promoted facilitated matters greatly. Nevertheless, the coverage achieved on a very moderate outlay has been quite phenomenal.

Mention has already been made of the fact that the object of the I.W.S. is international in scope. Whilst, therefore, London was chosen as headquarters, the period 1937-1939 saw promising progress made in obtaining international co-operation. Much useful promotion work was done in such countries as France, Belgium, Holland, Germany, Scandinavia, Italy and Switzerland, and the most cordial and co-operative relations were established with manufacturers in these countries and with the International Wool Textile Organisation. In the United States of America, a country with great potentialities for increased wool consumption, a major wool promotion and publicity campaign was embarked upon and American wool growers were organised to supplement this by raising funds themselves to do similar work.

When war broke out work on the continent of Europe was soon rendered impossible and, in fact, the I.W.S. had to face the question whether the circumstances created by the war justified a continuation of its work.

The peace-time structure of wool marketing was, of course, immediately brought to a complete standstill, but the experiences gained during the last war proved of great value in that respect. In the last war, the necessity of control was only gradually realised, and Wool Control in its ultimate form was the result of a long period of trial and error; and it was not before the autumn of 1916 that final agreement was reached on the purchase by the British Government of the Australian and New Zealand clips. This time, however, a Wool Control, under the Ministry of Supply, was in operation the day following the outbreak of war. An order was issued immediately bringing all business in wool, tops, noils and wastes to a standstill pending the inauguration of a system of allocating rations at fixed prices.

On October 14th, 1939, it was announced that the entire Australian and New Zealand wool clips had been bought by the British Government for the duration of the war and one year after at a flat rate, which meant an increase of about 30 per cent over the pre-war level.

In the case of South Africa, the British Government undertook, (1) to buy a certain minimum amount, and (2) to support the market by buying wool if the market price should fall below a certain schedule of prices. In August, 1940, this arrangement was modified and a new agreement between the United Kingdom and the South African Governments provided for the purchase of the entire South African clip along the lines of the agreements with Australia and New Zealand.

Following upon the purchases of the Australian and New Zealand clips in October, 1939, the whole system of control, which till then had been in a stage of transition, could be developed fully, and each stage from appraisal in the primary producing countries to distribution of supplies to the industry could be organised.

In the previous Appraisal Scheme, the number of types in the "table of limits" under which the scheme was carried out was 848, but in the present scheme the classification of the clip runs into approximately 15,000 types and sub-types. Each type is allotted a clean cost in keeping with its style, quality, length of staple, soundness and percentage of vegetable fault. A review of the first year of the war shows that despite this vast number of types and sub-types, the process of appraisal has functioned smoothly. The total value of Australian and New Zealand wools appraised during the season 1939/40 amounts to more than £76 million.

Data concerning the quantities shipped from the Dominions since the outbreak of the war cannot be disclosed, except for the monthly aggregate figures of Australian exports, which show that in the 1939/40 Australian season wool

exports totalled 933 million lb., compared with 922 million lb. in the previous season. These figures support the general opinion that the progress of wool shipments over that period has been very satisfactory.

It is expected, however, that the intensification of sea warfare and the necessity to divert shipping to the Near East for strategic reasons will adversely affect future shipments of wool like all other commodities.

These considerations, as well as the need for releasing the largest possible amount of labour and material for military and export requirements, have led the Wool Control to make further severe cuts in the raw wool rations available for the home civilian market. In addition, supplies of wool textiles to retailers in the home market have now been limited to 30 per cent of quantities supplied last year, i.e. hardly more than 20 per cent of average pre-war home consumption. This severe curtailment of home civilian supplies is coupled with the industry's co-operation with the Board of Trade's scheme for concentrating production in a number of "nucleus" firms and closing down all others, thus avoiding large-scale part-time working in the industry.

The closing of continental markets precluded operations there, and the restriction of the home market in Britain through these measures of rationing and limitations of supplies, in order also to divert production to war supplies, would have rendered the work of the I.W.S. abortive had it not been for the fact that its objective could still be achieved by concentrating on the promotion of exports of wool textiles. Consequently it concentrated on this.

The promotion of exports is a very vital matter in helping to finance the war, and the British Government had adopted active measures to organise industry to this end. Quite recently the wool manufacturing industry has been organised in this way. A levy on wool has been imposed and the National Wool Textile Export Corporation has been instituted to administer the fund so raised. The objects of this Corporation being absolutely identical with the work which the I.W.S. has already been engaged upon since war broke out, it is only natural that the two bodies sought ways and means to co-ordinate their work and thus to increase its effectiveness.

It is a matter of profound satisfaction that absolute agreement has been reached, and a working basis of active co-operation is at present being finalised.

The war-time export drive, including the promotion and publicity campaign, is responsible for the fact that despite the cessation of practically all trade with Europe, total quantities of British wool textiles exported to the few remaining overseas markets in 1940 were hardly below the 1939 level. Yet, despite this maintenance and even a possible increase of exports and the large calls made upon wool supplies for military purposes, stocks of wool are accumulating in the countries of production.

In the case of the Dominions, where all the wool has been bought by the British Government for the duration and one year thereafter, there is no immediate crisis. In the case of the South American wool-producing countries, however, the position is precarious. Being cut off from the European countries which were among the most important consumers of their raw materials, they now have to look towards Britain and the United States, and their ability to consume our goods depends on the extent to which we can consume theirs.

The United States are fully aware of the necessity of buying up the South American surpluses, and huge sums have already been devoted to this purpose. It may well be that such co-operation enforced by present circumstances may turn out to be the nucleus for a much more comprehensive scheme of economic co-operation of all raw material producers in the British Commonwealth of Nations and in the Americas.

Another important step in this direction is the recent decision to build up a reserve of 250 million lb. of Australian wool in the United States. The officially declared purpose of establishing this reserve is to provide "against a possible

emergency shortage of wool supplies in the United States." In view of the rapidly expanding American armament programme and the unprecedented increase in United States consumption of clothing wool during recent months, the U.S. Government may well come to draw more and more extensively on this reserve (which will always be replaced, maintaining the total of 250 million lb). There will, of course, also be large accumulated stocks of wool in the primary producing countries.

But over and above these present effects, the fact that at the end of the war there will be a wool reserve of 250 million lb in the United States may well have a far-reaching influence on the efforts to solve the post-war problems of wool marketing. If administered wisely, it should be some safeguard against a repetition of the disastrous slump after the last war. In fact, this reserve might possibly become a nucleus for a comprehensive "buffer pool" scheme along the lines of the Exchange Equalisation Fund and based on Anglo-American co-operation. The growing understanding of marketing problems in primary countries and the reasonable attitude of the majority of wool-growers, who prefer a secure modest profit to speculative gains, would certainly augment the chances of success of any such scheme.

The present unsettled state of world affairs makes it impossible and inopportune to work out clear-cut plans for the post-war world, all that can be done at the moment is to watch developments closely and with an eye to their possible post-war implications.

Yet, though detailed plans must be left to the future, there is a growing conviction that the economic reconstruction of the post-war world cannot mean a mere repetition of the erratic pre-war conditions, and that ways and means must be found to minimise the excessive fluctuations of raw material prices which have caused so much distress not only to the primary producers themselves, but also to all those dependent on their prosperity as well as to all those engaged in industry and commerce, whose calculations depend on raw material prices—in short, the entire economic structure of the world.

Many schemes have already been propounded. One such scheme, which has enjoyed considerable attention, is that made by L. St. Clare Grondona, in "National Reserves for Safety and Stabilisation," and discussed in a slightly modified form in the Royal Empire Society some months ago. The interesting feature of this scheme is that it proposed a joint plan of action for a large number of primary commodities, and in this way seeks to avoid the main cause of failure of marketing schemes for individual commodities, which have been established in the past.

Grondona proposed that in order to diminish price fluctuations in raw material markets the British Government should set up a corporation which would buy and sell a specified range of primary products at guaranteed prices, the purchase price being somewhat below, and the selling prices being somewhat above, the "average normal prices." These "average normal prices" would be fixed by an advisory committee representing buying and selling interests, and should be based on a "datum line" resulting from a careful review of prices in the past as well as conditions in the industries concerned.

Limitations imposed by time prevent me from presenting a more detailed discussion of this scheme. It certainly would be unwise to underrate its difficulties and dangers—the problem of how to fix the "average normal prices", how to make use of these limits once they have been fixed, the danger of attempting to control the market for a commodity without being in a position to control the markets for all near substitutes as well (e.g. an attempt to control the raw wool market without being in a position to control substitute fibres), problems of finance, etc.

I have mentioned this scheme specifically because it seems to me to contain an essential element which has been lacking in control schemes attempted in the past. It provides for graduated adjustment of relative values of a number of primary products. If in the form in which it was propounded it does not make provision for commodities produced outside the British Commonwealth of Nations it should be capable of modification to do so, if international developments do result, as the trend seems to be now, in a new world order based on active co-operation between the British Commonwealth of Nations and the United States of America.

I am conscious of the contentious and speculative nature of my remarks, not only on the subject of post-war international relations, but also on control of prices in general and of wool in particular, but it seems to me certain that international economic co-operation and effective control of industry are inevitable conditions in the post-war world.

## Reviews

**Reports on the Progress of Applied Chemistry**, Society of Chemical Industry, Clifton House, Euston Road, London, N W 1. Vol 25, 1940

These reports (belated owing to the war) have been issued without a break since 1916 and form part of the essential reading of every technologist anxious to keep in touch with all the published research in his own field. No matter in what branch of industry one is working there is always something to be picked up from what the other fellow is doing in his branch since his bye product may be your new valuable raw material. This is also probably true in the realm of ideas. Unlike the proverbial cobbler, the cellulose chemist should not stick to cellulose nor the wool chemist stick to wool.

The particular sections of immediate interest to members of this Institute are those on Fibres, Textiles and Cellulose. Protein Fibres are reviewed by Dr Whewell (pp 130-144) and Cellulose Textile Chemistry by Dr Marsden (pp 145-157). Dyestuffs users will want to read what Dr. R. Fraser Thompson has to say about developments in this field.

There is no report available on Spinning, Weaving or Textile Machinery, a gap which, it may be hoped, will be filled by the Textile Institute itself before very long. Meanwhile members will be grateful to the Society of Chemical Industry for this review of progress in textiles from the chemical and physical view points, though the price to non-members of the society, 16/-, is too high for those who only wish to read some of the reports. It is suggested that some arrangement could be made whereby the 80 pages of reports on textiles could be issued to non-members at a lower price than that of the full volume.

F. C. WOOD.

**"Mercerising"** by J. T. Marsh. Chapman & Hall, 32/-

The publication of this book is an outstanding event in the finishing industry, as it deals with an important branch of the industry in a comprehensive manner not previously attempted. It is over thirty years since any text book confined to this subject was published, and in that period many important researches have been carried out, a large proportion of which, including those from the Shurley Institute and the laboratory with which the author of the book is associated, have been published in this *Journal*.

The author shows originality in arrangement, by dealing with studies on individual cotton hairs first, followed by a technical section on the mercerising process, after which he reverts to detailed theoretical consideration, followed by a section dealing with absorption properties and a final section dealing with the efficiency of the process. This arrangement makes a very readable and interesting book, but involves dealing with some matters (e.g. lustre, and Coward & Spencer's research) in two sections, and the principle chapter on lustre is deferred to the last section in the book. An adequate index is, however, provided, and several of the chapters close with summarised references, e.g. to absorptive capacity measurements (p. 408) and tests of mercerising efficiency (p. 438).

The book begins in excellent style with an interesting historical section (27 pages) covering the periods of Mercer and Lowe. The section on cotton (64 pp) gives a complete account of researches into mercerising carried out on single hairs.

The technical section (pp 97 to 206) deals with yarn and cloth separately, followed by sections on machinery for mercerising yarn and cloth respectively. These sections are very useful and rather more detail in a few points would, if available, have been valuable. These are caustic soda consumption, relation between organic matter and settling in recausticising, with lime and soda, feel and cover in relation to fat content and drying conditions, shrinkage behaviour in relation to weave. Rope marking is not mentioned among the factors influencing the stage at which mercerising is carried out. The degree of scouring obtainable in mercerising needs mentioning in view of the large number of shirtings bleached without scouring. The elastic property of cloth mercerised loose might be mentioned. The dilution in washing necessary before relaxing the tensions is given as about 10 Tw. on p 164 and 15 Tw. on p 137.

The descriptions of machinery are very good and the illustrations are excellent and the reproduction very fine. Simili mercerising calender bowl pressures are stated in lbs per sq. inch, and are difficult to interpret. The mercerising mangle pressures are stated in tons without mentioning the width.

The following section on Rayon (pp 179 to 199) and linen (pp 200 to 206) covers the ground completely, even research results which have lost practical value owing to cold washing being faithfully recorded.

The next section (pp 209 to 284) deals authentically with cellulose constitution and reactions and the reactivity ratio of mercerised cotton. This is followed by another theoretical section (pp 285 to 356) on the reaction of cellulose and alkali.

A section (pp 357 to 420) is then devoted to absorption properties. Some of the earlier papers in this section have lost value as the drying conditions were not recorded.

The final section (pp 421 to 448) is called "Efficiency of the Process" and is concerned with the quality of the product. It deals with lustre and its measurement and the measurement of mercerising efficiency and it includes excellent photomicrographs. The difficulty of assessing the degree of mercerisation is brought out. Lustre is both complex and superficial, whilst absorption ratios, X-ray results and deconvolution counts are not directly related to lustre, or even to each other. The meaning of such terms as 40-70 per cent mercerisation (p 438) is therefore uncertain, but they are used by the author only in deprecating their value. Even the more general statement that cloth mercerisation is generally inferior to yarn mercerisation (p 94) seems to depend on the assumption of relationships between lustre and other measurable properties which are not established. Some reference to semi-mercerising would have been valuable in the chapters on estimating mercerising efficiency.

The book is almost free from misprints, only four minor ones being noticed (p 124-two, p 168, p 121), whilst the last sentence in the text (p 446) needs amending.

The printing and production would be a credit to the publishers even in peace time.

To research workers and students in the whole cellulose field, the book should prove invaluable, if only for the well considered account of all the researches of any importance on the subject. No such record of published researches is collected together elsewhere, and the record of fundamental work appears to be very complete, this point adding greatly to its value.

The book should prove indispensable to technologists controlling mercerising plant or other processes of cellulose treatment which include a mercerising stage.

L. THOMPSON.

# THE JOURNAL OF THE TEXTILE INSTITUTE

Vol XXXII

SEPTEMBER 1941

No. 9

## PROCEEDINGS

### NOTES AND ANNOUNCEMENTS

#### Midlands Section

##### JOINT MEETING WITH LEICESTER TEXTILE SOCIETY

The Midlands Section held a joint meeting with the Leicester Textile Society at the College of Art & Technology, Leicester, on Friday, 18th July. The chair was taken by Mr W J Lorrimer and a lecture on "Recent Developments for the Production of Unshrinkable Knitted Articles", was given by Mr W A Edwards, A T I. This was the opening meeting of the Midlands Section programme.

Mr Edwards discussed the chief methods now available, including those recently introduced for controlling the production of the unshrinkable finish on knitted woollen goods. After describing the behaviour of the wool fibre towards acids, alkalis and oxidising agents, Mr Edwards explained the conception of hydrogen ion concentration and the application of pH measurement to the control of the activities of solutions of acids and alkalis. After considering the phenomena of detergency, Mr Edwards dealt with the use of soaps and fatty alcohol sulphates in wool scouring, preparatory to describing the importance of control in the wet and dry "chlorination" treatments for unshrinkability. Reference was made to the process in which sulphuryl chloride is the active agent.

Finally, Mr Edwards stressed the importance of control by testing the finished material and indicated practical methods for the identification and assessment of fibre damage.

##### JOINT MEETING WITH COVENTRY TEXTILE SOCIETY

On Saturday, 13th September, the Midlands Section held a joint meeting with the Coventry Textile Society at the Technical College, Coventry. Mr H A Turton, Chairman of the Coventry Textile Society, presided, supported by Mr W Pritchard, Chairman of the Midlands Section.

The subject "From Fibre to Fabric" was very ably dealt with by Mr G S Robinson, Managing Director of Messrs G Ingham & Co Ltd, Greetland, Halifax, and a most interesting film was shown dealing with wool from the sheep's back to the finished garment.

It is understood that this film was entirely produced by the lecturer with the exception of the introductory shots taken on an Australian sheep farm. By its medium the audience was conducted through every process of worsted manufacturing from the shearing of the sheep to the finished garment as displayed by mannequins at recent British Industries Fairs.

A brief introductory talk was given by Mr Robinson prior to showing the film, and he also kept up an interesting running commentary during the exhibition.

Full advantage was taken by the members of the lecturer's invitation for questions, and enquiries were particularly numerous for information on present-day applications of Fibro as a substitute for wool. The lecturer also had a most interesting display of samples corresponding with and depicting the numerous manufacturing operations as shown in the film.

Mr W. A. Edwards, of Loughborough, moved a very warm vote of thanks to Mr Robinson, and complimented him on the production of this very excellent and instructive film.

This incidentally was the opening meeting of the Coventry Society's most attractive programme of lectures which has been arranged for the coming Winter Session.

## Yorkshire Section

### PROGRAMME 1941-42

- 1941.
- Thursday, 2nd Oct., 7 p m. .. Prize Distribution by G. H. Thompson, Esq., J. P., F.T.I., President of the Textile Institute, followed by Address and Smoking Concert. Short address by Dr C. J. T. Cronshaw, B.Sc., F.I.C., M.I.Chem.E., F.T.I., F.R.S.E., President of the Society of Dyers and Colourists.
- Saturday, 11th Oct., 3 p m. Joint Visit to British Cotton Industry Research Association, Shirley Institute, Didsbury, Manchester.
- Thursday, 16th Oct., 7 p m. "Gallup Survey" L. Moss, Esq., British Institute of Public Opinion.
- Thursday, 20th Nov., 7 p m. "Textile Architecture" Dr F. C. Toy, D.Sc., F.Inst.P., F.T.I., Deputy Director of the British Cotton Industry Research Association.
- Thursday, 18th Dec., 7 p m. Lecture by a member of the Wool Industries Research Association. Details later.
- 1942
- Thursday, 15th Jan., 7 p m. "Banking in Relation to Imports and Exports" J. S. Kipling, Esq., Cert. A.I.B., A.C.I.S.
- Thursday, 19th Feb., 7 p m. "A.T.I. Evening"
- Saturday, 14th March, 3 p m. Joint Visit to Wool Industries Research Association, Torridon, Headingley, Leeds.
- Thursday, 19th March, 7 p m. Ladies' Evening, "Colour Photography"
- Thursday, 26th March, 7 p m. Annual Meeting

Meetings will be held at the Midland Hotel, Bradford, and W. Garner, Esq., M.Sc., A.I.C., F.T.I., will be chairman.

## Institute Diplomas

Elections to Associateship have been completed as follows since the appearance of the previous list (July issue of the *Journal*).—

### ASSOCIATESHIP

GERHARD WILHELM EISIG  
RONALD WOOD

### Institute Membership

At the September meeting of Council the following were elected to membership:—

#### *Ordinary.*

- T. Berry, 50, Candren Road, Ferguslie, Paisley (Asst Chemist, Chemical Inspection Dept, Ministry of Supply)
- H H Busfield, "Lyndhurst", Rufford Drive, Yeadon, nr Leeds (Woollen Mill Manager)
- V H Cooper, Boulevard Works, Radford, Nottingham (Principal, Vernon H Cooper Co)
- J Creswick, 47, Norreys Road, Didcot, Berks (Principal Viewer, Physical Testing (Textiles) and Official Photographer of the Royal Army Ordnance Depot).
- R W. Johnson, B Sc. (London), Test Laboratory, Ministry of Works and Buildings Store, Royal Mill, Droylsden (Inspector of Stores)
- J E Leigh, 48, Brook Street, Oldham (Cotton and Cotton Waste Merchant)
- C H Leland, Retford, Woodland Avenue, Hazel Grove, Cheshire (Textile Expert and Salesman, Tragasol Products Ltd, Hooton)
- W H Richardson, Wildspur Mills, New Mill, Huddersfield (Director and Works Manager)

#### *Junior*

- L W R Hill, 16, Duchy Avenue, Heaton, Bradford (Student, Leeds University).
- F H. Lisle, 23, Devon Drive, Sherwood, Nottingham (Chemist's Assistant, Dyeing Laboratory, British Celanese Ltd).
- H Meier, c/o Fabrica de Tejidos, "La Union", Lima, Peru (Assistant in Textile Mill)
- J Menkart, Oakwood House, Grove Lane, Leeds 6 (Textile Research Student, Leeds University)
- I R Thornton, White Bungalow, Lambley Lane, Burton Joyce, Notts (Student in Textiles).

## Reviews

**"Physical Chemistry of High Polymeric Systems"**, by H Mark Interscience Publishers Inc New York Price 39/- net Obtainable in the United Kingdom from H K Lewis & Co Ltd, 136, Gower Street, London, W.C.1

**"Collected Papers of Wallace Hume Carothers"**, by H Mark and G. S. Whitby. Interscience Publishers Inc New York Price 51/- net Obtainable in the United Kingdom from H K Lewis & Co Ltd, 136, Gower Street, London, W C 1

One of the most striking features in the development of physics and chemistry within the last decade has been the rapid growth in our knowledge of macromolecular systems, both natural and artificial. The subject was chiefly developed in its initial stages by the organic chemists, but its modern aspects are almost completely physical and, in fact, form one of the most fruitful fields of current physico-chemical research. With the rapid increase in the industrial importance of many of the high molecular substances, a large body of technical knowledge has come into being concurrently with the more academic studies of the subject with the result that the literature on high polymers is now extremely scattered. Hence, the need has been felt for some time by workers in this country and in America for a connected account in English of recent advances in the field, especially as the existing text-books have been more concerned with its technical and industrial development. The books under review are the first two of a series written specifically to fill this gap.



The first volume is in the nature of a memorial to Wallace Carothers and consists of his collected papers on polymerisation, covering the years 1929 to 1936. It would be out of place here to give any biographical account of this man's almost meteoric career; it has been done admirably by Roger Adams in the introduction to this book. The collected papers divide themselves naturally into two groups. One of these is concerned with the researches on acetylene polymers and their derivatives which finally led to the commercial production of "Neoprene", one of the most successful synthetic rubbers to date, the papers here mainly show Carothers as a leader in organic chemistry, the field in which he received most of his formal training. The remaining studies are concerned with polycondensations and ring-formation, out of this work has come the synthetic textiles of the "nylon" type. Here is shown Carothers not only as a brilliant organic chemist, but also as a worker with a penetrating insight into the physico-chemical problems of these large molecules. It was probably this combination of qualities more than anything else which gave him his pre-eminent position in American chemistry.

The title of the second volume in "High Polymers" is at first sight somewhat of a misnomer, and those who are expecting from Professor Mark a complete account of the applications of modern physical chemistry in all its ramifications to macromolecular systems will probably be rather disappointed. The author, however, takes the view that the properties of high polymers will be ultimately explained on the same basic principles as those used for elucidating simpler systems and that, before any attempt can be made to understand high polymers, a thorough understanding of these principles must be acquired. With this aim, Professor Mark has written a book which is not only an invaluable introduction to high polymer chemistry for the specialist in the subject, but which also is a unique text-book for the general reader on certain aspects of modern physical chemistry.

As might be expected from the author's reputation, structural methods and results occupy several sections and there are also informative chapters on the internal motions of molecules, the various types of valency forces and the properties of binary mixtures. Throughout, the aim has been first to clarify general principles and then to indicate their special application to long-chain molecules. The section on the important topics of osmotic, viscosity and solubility phenomena give a brief but valuable summary of the recent work done on the Continent, which is not yet very well-known in this country, in fact, this account is the first authoritative one to appear in English. It is hoped to expand these sections into separate volumes in the series to be published later. The same is true of the chapter on kinetic phenomena.

Both volumes are well produced and can be strongly recommended, especially that of Mark, but the appeal of both to the general reader in this country will probably be severely reduced by their high price, nevertheless, the specialist in the macromolecular field will await succeeding volumes with great interest.

R F TUCKETT

## General Items

### Additions to Library

The following books have been received.—

**Cotton Year Book, 1941.** Published by Textile Mercury, Ltd, 41, Spring Gardens, Manchester 2

**Wool Year Book, 1941.** Published by Textile Mercury, Ltd, 41, Spring Gardens, Manchester 2

### Identification of Fibres

Much interest has been shown by members of the Institute and others in the charts and notes dealing with the Identification of Fibres in the June issue of the *Journal*. There has been a demand for extra copies for this section and reprints are now available. The charts and notes in pamphlet form can be supplied at 1/- a copy, and a set of the charts only, which could be framed, are available at 6d a set from the Acting Secretary of the Institute.

# THE JOURNAL OF THE TEXTILE INSTITUTE

Vol. XXXII

OCTOBER 1941

No. 10

## PROCEEDINGS

### NOTES AND ANNOUNCEMENTS

#### Textile Institute Diplomas

Elections to Fellowship and Associateship have been completed as follows since the previous list (September issue of the *Journal*) —

##### FELLOWSHIP

JOSEPH MALLINSON McISAAC,

Principal, Wilts County Textile School, Trowbridge

##### ASSOCIATESHIPS

HARRY MILTHORP APPLEYARD

JOHN COOPER

WILLIAM GODDERIDGE

FRED RAYMOND STAFFORD

#### Institute Membership

At the October meeting of Council the following were elected to membership.

##### *Ordinary*

- E Boothroyd, 106, Noel Street, Nottingham (Technical Dyer)
- J B Gartside, Crimble Cottage, Bamford, Rochdale (Cotton Broker)
- E C Harrold, The Mills Equipment Co Ltd, Fountayne Road, Tottenham, London, N 15 (Manager of Fabric Department)
- F Howlett, 49, Parrswood Avenue, Didsbury, Manchester (Research Chemist, British Cotton Industry Research Association)
- H Kitchen, 278, Birchfield Road, Birmingham, 20 (Chief Chemist, Cotopa Ltd, Leeds)
- R Schueller, 21, Vivian Way, London, N 2 (Departmental Manager)
- A Thompson, 1, St Johns Avenue, Chaddesden, Derby (Head of Textile Department, Derby Technical College)

##### *Junior*

- F Anderson, 203, Windhill Old Road, Thackley, Bradford ("Top" Production Manager)
- F Ashworth, Stanley House, Philips Park Road, Whitefield (Student, Manchester College of Technology)
- J Dean, 44, Towncroft Avenue, Middleton, Manchester (Chemist).
- H R Sutcliffe, 50, Wharf Street, Sowerby Bridge (Apprentice Technical Foreman Dyer).

# Examination in General Textile Technology, 1941

## REPORT OF EXAMINERS

The examiners have pleasure in recording that this year's candidates showed an appreciably higher standard in English composition, and in the presentation of the matter of their answers, than those of previous years

The effects of war conditions were, the examiners believe, to be seen in the lower average level of knowledge displayed the performances of a few outstanding candidates are therefore worthy of special praise

The examiners again find evidence of inability on the part of candidates to relate fundamental mathematics, physics and chemistry to textile operations and processes the teaching of technology may well be judged by its success or failure in enabling students to discover and to use such relations

Misunderstanding by some of the candidates of the meanings of technical terms and phrases again emphasises the importance of agreed names and definitions in the industries.

## SECTIONS I AND V OF SYLLABUS

10.0 a.m. to 1.0 p.m. —28th May, 1941

*Candidates to answer THREE questions in EACH Section*

### Section I—Fibres and their Production

- (1) Describe how the structural features of cotton hairs and wool fibres are determined by their mode of growth.
- (2) Compare the manufacture of viscose fibres with the manufacture of nylon, indicating the purpose of each of the various processes you describe
- (3) Enumerate and discuss briefly the various fibre qualifications necessary for the production of satisfactory yarns. Compare cotton and flax in respect to these factors
- (4) Discuss the physical properties of Asbestos, Kapok and Nylon and explain why these materials are of special importance at the present time.

### Section V—Analysis and Testing of Raw Materials, Yarns and Fabrics

- (5) What do you understand by the term "relative humidity"? Describe how this can be ascertained How does the relative humidity of the atmosphere in which (a) cotton, (b) worsted yarns have been stored immediately prior to testing affect their tensile strength and elongation.
- (6) A two-and-two twill cloth is woven in which the weft is a mixture yarn consisting of 90 per cent of  $2\frac{3}{4}$ " merino wool and 10 per cent of 2" staple Fibro spun on the worsted principle The cloth is piece dyed Navy for wool only. By mistake an odd bobbin of weft is used in which the 10 per cent. admixture of staple fibre is of 4" staple instead of 2". What will be the consequent appearance of the cloth? Give reasons for your answer.
- (7) State and explain the effect of length of test specimen on the apparent strength of yarns.
- (8) In what ways may the crimp (regain or take-up) in its constituent yarns influence the character of cloth? Describe the method you would employ to obtain an accurate measure of crimp.

- (9) Describe how, when sampling and testing, provision may be made for the natural variability of textile materials. Show by examples how the probable effect on the yarn irregularity of the processes employed in your production may be calculated.

## SECTIONS II, III AND IV OF SYLLABUS

2 30 p.m. to 5 30 p.m.—28th May, 1941

*Candidates to answer TWO questions in EACH Section*

### Section II—Conversion of Fibres into Finished Yarns

- (1) In the production of normal types of folded yarns from cotton singles it is usual to assemble the required number of ends on a spool for the creel of the twisting frame. Give the reasons why this procedure is usually more satisfactory than twisting direct from the singles, and say whether the same procedure may, or may not be satisfactory in the production of a union yarn composed of one thread of cotton, and one thread of some other type of single yarn.
- (2) With the aid of simple diagrams show how twist is inserted into ring, mule and flyer spun yarns. By what means is drag imposed on the yarn in these methods of spinning?
- (3) Describe the chief characteristics of warp, weft and hosiery yarns of either cotton or wool. Why are these characteristics required and how are they obtained?
- (4) Explain why yarns are nearly always spun from a blend of raw materials. Describe the methods employed to obtain a thorough mixing of the blend in the case of (a) woollen yarns and (b) either cotton, or flax, or worsted yarns.
- (5) Discuss the influence of irregularity in yarn thickness on the distribution of twist. Explain how periodic variations in twist are produced in mule-spun yarns, and indicate the kind of fault in fabrics to which they give rise.

### Section III—Conversion of Yarns into Fabrics, and Fabrics produced by Special Methods

- (6) Compare the two standard Dobbies, discussing the special advantages or otherwise of each, also the type of cloths for which they could be most usefully employed.
- (7) Explain how openwork fabrics such as net or lace are made on (i) a woven basis, (ii) a twist lace principle, (iii) a knitted basis. Give drawings showing the fabric structure in each case.
- (8) Explain how the operations of shedding, picking and beating-up should be related to each other to produce a well covered plain woven cloth.
- (9) Point out the factors which determine whether weft yarns require preparation between spinning and weaving. Give examples of yarns which require preparation and of others which are woven as spun. Describe the operation of winding weft for the shuttle, stating the kind of yarn assumed.
- (10) Describe the arrangement of mechanism fitted to a power loom to prevent the loom from working when the weft is broken or the whole of the yarn unwound from the pirn or shuttle peg.

### Section IV—Conversion of Fabrics into Finished Materials

- (11) Coloured cotton yarn is sometimes woven along with grey cotton yarn in manufacturing multicolour fabrics which are subsequently bleached. Mention the chief classes of dyes used for the coloured yarn and give an outline of the method of application of a suitable dye
- (12) Woollen vests and cotton shirts may shrink as a result of washing treatments. Give a probable explanation of the cause in each case. Describe how the shrinkage may be prevented or minimised in the production of the material for *one* of these garments.
- (13) What do you understand by "mercerisation"? To which of the textile fibres is it appropriate? Explain why in your opinion it is not suitable for application to each of the other more important textile fibres.
- (14) Write a short essay on the possible uses of synthetic resins in the production of finishes on textile fabrics
- (15) A manufacturer wishes to augment his supply of wool by blending with it an equal weight of another fibre. What materials suitable for this purpose are available? Selecting one of them describe a method of producing a black, fast to washing, on yarn spun from the mixture of wool and wool diluent.

## ANALYSIS AND TESTING OF TEXTILE MATERIALS

### Section A

Monday, April 28th, 1941

*Three hours to be allowed for this paper.*

*Not more than FIVE questions to be attempted. The answer to each question attempted must be commenced at the top of a right-hand page in your answer book. You must write your examination number at the top of each page upon which you begin an answer.*

- (1) With the aid of diagrams, show the microscopic appearance of the following fibres.—Mohair, mature cotton, virgin wool, mungo, mercerized cotton, flax and hemp
- (2) Which countries are the greatest producers of cotton, flax, wool, silk, continuous filament rayon and staple fibre rayon? Outline very briefly the reasons for this geographical distribution
- (3) Name, in their order of importance, the chief members of the bast fibre group. Outline in each case the method of manipulation in preparation for market
- (4) Describe a method of preparing cross sections of textile fibres. Assess the method critically in respect of speed, labour involved, the quality of the results, and any limitations the method may be expected to have.
- (5) Describe how changes in moisture content affect the strength and extension of cotton, wool, acetate rayon, viscose rayon and linen yarns. How is the position affected if the materials are subjected to prolonged exposure out of doors?

- (6) Define *Relative Humidity*, and explain how it is affected by changes in temperature. Give a brief description of three different types of hygrometer, indicating the underlying principle of measurement in each case
- (7) What do you understand by the term "hysteresis"? Describe any examples of hysteresis phenomena in connection with textile fibres with which you are familiar, and indicate their significance in connection with textile testing
- (8) Compare the principles of the balances used in counts testing. What balance would you recommend for yarn wrapping in a cotton mill spinning 10's to 40's counts, and why?
- (9) Describe the construction and use of any strength testing machine with which you are familiar, and give your opinion as to how far this machine fulfils the ideal requirements of a strength tester

### Section B

*Wednesday, April 30th, 1941*

*Three hours to be allowed for this paper*

*Not more than FIVE questions to be attempted. The answer to each question attempted must be commenced at the top of a right-hand page in your answer book. You must write your examination number at the top of each page upon which you begin an answer.*

- (1) Describe the methods you would employ (a) to determine the percentage of each constituent in a wool and cotton union shirting, (b) to distinguish between acetate artificial silk and real silk
- (2) Describe briefly the methods you would use to determine (a) the fibre length distribution, (b) the mean diameter of a consignment of *either* cotton or wool fibre. What importance would you attach to your method of sampling?
- (3) Discuss the difficulties in making accurate measurements of yarn twist. Illustrate your answer by reference to the testing of single and folded yarns
- (4) Explain with the aid of an example how you would proceed to determine the number of tests needed to give a result (Arithmetic Mean) of any specified degree of accuracy.
- (5) What are the distinguishing features of the following cloths.—
  - (a) Cheviot overcoating,
  - (b) Saxony costume cloth,
  - (c) Botany worsted suiting,
  - (d) Rayon lining?

Your answer must include the materials used, yarn structure, type of finish generally applied, and the handle of the finished fabric

- (6) Cotton raincoat cloths differ considerably in their permeability. Discuss this in detail, taking into consideration all the factors involved in the making of such fabrics
- (7) Explain the possible causes of colour defects which may be found in bars running weft way across the piece in yarn dyed gabardines.

## Yorkshire Section

### OPENING MEETING AND PRIZE DISTRIBUTION

The Yorkshire Section commenced its winter programme with a smoking concert and prize distribution held in Bradford on Thursday, 2nd October. The meeting was well supported and the Chairman of the Section, Mr W Garner, was in charge of the proceedings. He said "This is the opening meeting of the third war-time session, and I hope that the example of last winter will be followed with regard to good attendances. Despite the fact that last winter was a war-time term there was actually a record number of attendances, and any falling off in numbers was due, not to war conditions, but to the exceptionally heavy snow-falls which prevented many of those members living outside Bradford from being present.

"It is especially noteworthy that at this opening meeting, sitting at the same table, are the Presidents of those two societies which mean so much to the textile industry, I refer to Dr Cronshaw, President of the Society of Dyers and Colourists, and Mr Thompson, President of the Textile Institute. These two societies are closely allied, and it is a happy symbol of their conjunctive work that we are pleased to have their respective presidents with us to-night. Mr Thompson has very kindly consented to come and present the prizes awarded for the textile design competitions. It seems to me that textile design imposes more limitations upon the artist than almost any other form of art. The effect of limitations of form, technique, and material upon the artist has for long been a matter of interest to me, and it is worth noting that some of the greatest artists have laid down self-imposed and apparently unnecessary limitations. Thus the poet, who could if he chose, write with no more limitations than words and grammar impose, invents severe, rigid, and uncompromising rules, which he must obey, of form, rhyme and rhythm. It may be that these limitations act in the same way as a dam across a river, creating a store of power which, when the limitation is overcome, brings out new heights of achievement which would otherwise fritter itself away. Or it may be that the obeying of limitations often brings about chance effect; and the wise artist well knows how to use what Charles Morgan calls 'the miraculous harvest which may spring from chance'. A third reason for the welcome acceptance of limitations by the artist is that it enables an artist to discipline, with a discipline which is enjoyed, an imagination otherwise too free. Men of impulsive imagination as most artists are, rarely do easy things well. They require difficulties to compel them to reach their full power. We all know that at times an exceptionally severe problem has arisen which has called out all our ability and strength, and sometimes if we are successful we look back upon what we have done with considerable surprise, as if someone else had done it, well knowing it to be beyond our normal skill. The writing of verse in the form of a sonnet, the composition of music in sonata form, and the production of a work of art in a design suitable for production as a textile fabric; with its limitations of fibre, colour, weaving and printing can be made a mechanism to compel the artist to do something great."

Mr Thompson, before distributing the prizes said "The Yorkshire Section of the Institute is very large. It is not the first time that the President of the Institute has come to the opening night and I regard it as an honour that I am invited to be present this evening. This year we have had fewer competitors, but the work submitted by these competitors is extremely good. Many of the young people of to-day are now in the forces, and in view of the scarcity of opportunity for study and the time spent in those voluntary services undertaken by most competitors, it augurs well for the textile industry and the people of Yorkshire in particular that such creditable efforts have been made. During the past year we have lost the founder of these competitions, Mr John Crompton.

His great work will long be remembered. Although his passing is a matter for regret, yet the rate of progress has not been retarded. Others have tried, and succeeded, in keeping the torch alight, and a tryer is always welcome. He fills the past with romance, the present with satisfaction, and the future with zeal. These tryers are with us this evening and the result of their labour is here for us to see. In their hands the future lies, for they will be the great men of the textile industry in the days to come. Much of the post-war reconstruction will be done by the youth of to-day. We older men will be unable to reorganise the textile industry as it needs to be reorganised, for we shall be too eager to remodel it upon the old lines, the lines which have become a habit with us during many years. It is these young people who will come to it with a fresh outlook, with more scientific ideas and, as we can see by these entries, a capable practical knowledge which will enable them to carry through their scientific thoughts in a practical manner thus giving a valuable contribution to progress."

The successful Yorkshire competitors then received their awards from the President.

The Chairman, at this stage, introduced the principal guest of the evening, Dr C J T Cronshaw, President of the Society of Dyers and Colourists. He explained that the Society had been very fortunate in its choice of Presidents, and that the Yorkshire Section of the Institute was very pleased to welcome Dr Cronshaw, who was now serving his third term as President.

In expressing his thanks for the warm welcome extended to him, Dr Cronshaw said "It has been mentioned that this is the first time that a President has taken office for a third term, but in my case this is due to the war. Mr Garner has said some kind things about the amicable relations existing between the Society of Dyers and Colourists and the Textile Institute, and I have always thought of the two societies as twins, working side by side.

"I would like to join Mr Thompson in congratulating the prize-winners. Times are difficult and habits have changed, with study and powers of concentration at a disadvantage. It is hard to settle down and study, and many congratulations are due to those who have done so. Thinking and planning must be done until it hurts, and it is only through resource that we can do it. Like myself, many of you have probably found your way to Old Trafford at some time, and Yorkshire has always shown resource in its battles there. We know that Yorkshiremen have this resource, and that they can and must do this planning and thinking.

"Mr Thompson has referred to the reorganisation of the textile industry, and one of the major changes which has already taken place is the employment of women in industry. Industry has been too reluctant to use women up to the maximum extent and we shall have to find that once in they won't go out, and that we shall not want them to go either.

"However, all this really goes to show how pleased I am to be invited, especially as I happen to be a Fellow of the Institute."

Mr H Hardy proposed a hearty vote of thanks to Mr Thompson and expressed the pleasure of the Yorkshire Section in having the President of the Institute at its opening meeting.

Mr F Smith proposed a hearty vote of thanks to Dr Cronshaw and said that the Yorkshire Section was honoured by having as its guest the President of the Society of Dyers and Colourists.

The meeting closed by Mr G Haigh thanking Mr Garner very sincerely, on behalf of the Yorkshire Section members, for the hospitality extended to them by the Chairman. Mr Haigh wished him every success in his year of office.

The successful fabrics, yarns and designs submitted in the competitions were on view before the meeting commenced.

During the evening there were several items of entertainment which were keenly enjoyed by the members present.



## Lancashire Section

### FILM, PRIZE DISTRIBUTION AND LECTURE

The Lancashire Section had a most interesting meeting in Manchester on Saturday, 20th September. The meeting opened with a sound film in colour, entitled "Queen Cotton", which had been produced by the British Council in conjunction with the Cotton Board. Mr H. E. Wadsworth, a representative of the Cotton Board, introduced the film and said that it was being shown in many places abroad with the object of bringing the cotton trade of Lancashire to the notice of foreign countries. The talking commentary had already been translated into five languages.

After the film, the presentation of prizes to successful competitors in the Lancashire Area took place. Mr B. Hesketh, who acted as Chairman of the meeting, referred to the late Mr John Crompton, whose generosity and enthusiasm had made possible the Competitions for textile design, structure and yarns which were held annually by the Institute. The Competitions were created in memory of Mr Crompton's son, Lieutenant Harry Dent Crompton, who was a pilot killed in action during 1916.

The Chairman explained that it had been the intention of the President, Mr G. H. Thompson, to present the prizes, but due to indisposition Mr. Thompson was unable to attend. Mr Cleveland Belle, Director of the Colour Design and Style Centre of the Cotton Board, kindly distributed the prizes in place of the President. The prize winning entries from all the Competitions were on view and much interest was shown in the work which was of a high quality.

Mr Belle then gave an address on "Design Fashion and the Textile Industry". He opened by discussing the two essential features that determine the sales value of textile merchandise—quality and appeal. In doing so, he laid claim to the greater share of attention for the second of these, arguing that in these days a satisfactory standard of quality is very largely taken for granted by the purchasing public and that in any case great durability is no longer looked for as it used to be in times past. "Any retailer will tell you that fifty per cent of the complaints he has from his customers are because they do not like the colour, or the design, or the cut, or the fit, rather than because the intrinsic quality of the article is not as high as they expected. The selling factor to-day is the right colour, the right line, the right pattern—in other words, it is Fashion. If any further proof is needed, look at the retailer's stocks. In our grandmother's time stockings were sold in black, white, grey, brown and navy and that was about all. Nowadays a line of stockings will be dyed in thirty or forty colours. A coat showroom is packed with coats of one colour at the end of the season. What is the reason? There is nothing wrong with the coat, but the colour has not sold this season."

Mr Belle then went on to point out that the importance of fashion as a factor in sales value begins to grow as soon as the purchasing power of the community rises above the bare subsistence level, and cited the recent history of Russia as a contemporary example of such a development taking place in an unusually short space of time. "A woman needs clothes to keep her warm—that is a prime need. But give her a little more money, a little more command over goods, let her be certain that she is to be warm—that she can satisfy her primary need and she will then begin to indulge her taste, choice will enter into the calculation, she can afford to discriminate. Give her still further command over goods and she will forget her primary need almost altogether and concentrate on indulging her taste. Now this ability to exercise taste, to vary the monotony, has been made possible by two factors. One is the general rise in the standard of living of the ordinary person, and on the other hand, you have the influence of mass production tending to make things cheaper. Fashion has an economic basis."

"Before we go on to inquire where fashion comes from, let us note that there is nothing new in this fashion thing. Changes in dress and personal adornment, in furnishing and furnishings, have been going on through history. What is new is the rapidity with which style changes and the fact that it so quickly affects the desire of the whole buying community whatever their economic level. Where then does this thing that is fashion come from? Even the clever designer cannot create a fashion at will. He cannot sit up all night with a damp towel round his head and get up in the morning and create a new trend. I sometimes hear people talk as if a new fashion can be created at will—merely by thinking about it. It can't. It goes almost without saying that the fashion designer must possess the designing talent, but he must also have something else. He must be acutely conscious of the world in which he lives. He must be up-to-date in the sense that he is conscious of the trends of modern life. Fashion is an expression of the world in which we live, it is an expression of what we feel.

"When we want to know what life was like in former times we spend a great deal of time finding out what clothes people wore; what ornaments they carried; what their homes were like, because all these things are the expression of the times.

"Fashion is, in a sense, 'in the air' and the clever designer is the person who feels the atmosphere and can interpret it. No body of designers can thrust an idea on the public and make it fashionable unless the public are ready for it. James Laver, who is one of our best writers on fashion, says it seems as though there lies some mysterious satisfaction in being in harmony with the spirit of one's age. No designer can force an idea until the public is ready for it. Patou, after the last war, tried to force women to put the waist higher. He was many seasons before the time, and he lost money. Many designers tried to force the long skirt two years before it began to be accepted. They could foresee the trend too far in advance.

"I have so far suggested that colour and design are the chief selling factors in fabrics to-day, and that it is not just whether the colour and design are aesthetically admirable, but whether they are in fashion that is important. This fashion element counts whatever the grade of public you are catering for. I have tried to suggest that this fashion thing—this desire for change or, to put it another way, this desire to be in tone with one's times, is quite fundamental. If the designer is to have this fashion quality, which is essential if he is to be of use, then he must know more than the principles of design. He must know more than the technical process involved in cloth manufacture. He must know more than the economics of manufacture. More than all these he must be acutely aware of the spirit of the times."

Mr Belle then indicated the various ways in which this consciousness or sophistication may be acquired and developed by attending important art exhibitions, mannequin parades; theatres, and particularly the ballet; by travel, and generally by mixing with and observing the tastes of that class of society whose economic level permits the greatest freedom of choice in furnishings, adornment and dress.

Turning finally to a consideration of the future of the textile trade in this country, the lecturer forecast a more intense struggle for foreign trade under post-war conditions. "In the past we have been a creditor nation, in the future we may be a debtor country, and if so, everything we buy from overseas will have to be paid for in goods, and unless we are to have a very low standard of living indeed, our exports will have to be bigger than they have ever been before.

"How then are we to compete in the world's markets? It may be, I might almost say it will be, increasingly difficult to sell plain cottons, and we must be prepared to give more and more attention to selling fabrics on their fashion value. I am not decrying the need for technical improvements and scientific

research, these are always important, they are even important from a fashion point of view—new textiles, new weaves, new finishes, cloths with new draping and working possibilities. But I do say that more than ever before we shall have to give attention to fashion.

“Through the Cotton Board’s Colour, Design and Style Centre, we hope to fill a long felt want in Lancashire in this respect. We are studying the making of fashion, collecting news from every available part of the world, assisting firms in the evolution of new fabrics, helping them to get in touch with new designers.

“You may ask why the Centre should operate during war time, when fashion must of necessity become a secondary issue, indeed when fashion textiles themselves are products of secondary importance.

“I have talked of the probable need for exports after the war to help to pay for the imports we shall need. I may remind you too, of the millions of munition workers and members of the Forces for whom work must be found. It is essential that Lancashire must be able to start making and exporting as soon as possible when the war is over, and moreover, making and exporting stuff that will sell—textiles with a fashion appeal. It is, therefore, of the utmost importance, with travelling abroad made impossible, with it even being difficult to get foreign periodicals, that there should be a central source of information about what is going on in the outside world. We must know the products of our competitors as they appear, and we must know where they have been selling them. The importance of having access to overseas publications is unquestioned. You will find them at the Colour, Design and Style Centre’s premises which are now nearing completion. But there is another point of importance. That too, I submit, is part of the business of the Cotton Board’s Colour, Design and Style Centre—by doing everything it can to help the designing of whatever cotton is being produced, and finding means of noising this news abroad, maybe by sending patterns, maybe by photographs, but insisting all the time that there is still such a thing as British cottons, and that we are working on the business of keeping them alive and up-to-date even if the bulk of our industry is now actively engaged in the war effort. Then when the time comes again that we are able to go all out for export, not only will the cotton industry be ready to step right out, but we shall be selling to a world that has not forgotten the fabrics of Lancashire. We of the Colour, Design and Style Centre intend to see, to the best of our ability, that whatever we can do to ensure for the cotton industry of this country a place in the sun of the world’s fashion markets immediately after this war, will be done.”

At the close of the talk Mr J Greenwood proposed a vote of thanks to the speaker for the very appropriate address which had been given in conjunction with the Prize Distribution. Mr F I Sharp seconded the vote of thanks and was supported by the Chairman. Mr Belle replied and expressed his appreciation of the kind reception he had received.

## Midlands Section

### PRIZE DISTRIBUTION

On Tuesday, 7th October, a meeting of the Midlands Section was held at the Leicester College of Technology and Commerce, when the prizes in connection with the Knitted Fabrics (E) Competition were presented to the successful candidates.

In the absence of Mr W Pritchard, F T I, owing to illness, Dr Edwin Wildt presided, and the prizes were presented by Councillor P A Bentley.

In his introductory remarks, Dr Wildt emphasized that, looking forward to post-war days, we should have a hard battle in front of us to maintain a premier

position in the textile industry in face of international competition, he suggested that competitions such as those arranged by the Textile Institute were extremely helpful in providing the correct mental equipment of the personnel which would have to contend with the world-wide competition of the future.

Councillor P. A. Bentley, M I Mech E, presented the prizes, and in congratulating the competitors pointed out that the quality of the specimens submitted was uniformly high. He gave suitable words of encouragement to the students and prize-winners, and expressed the hope that the quality of the entries would not only be maintained but would be improved. The awards were then presented to the successful candidates.

Mr L. W. Kershaw, B Sc, A M I C E, F G S, moved a warm vote of thanks to Councillor P. A. Bentley, not only for his kind attendance at this function to present the awards, but also for his generosity in providing the prize money.

In supporting this motion, Mr N. Tunstall, H M Inspector of the Board of Education, expressed the view that the modern knitting machine with all its intricacies was valueless without a capable designer, and he applauded the value of the competitions as being instrumental in discovering such talent.

Mr Tunstall also expressed a wish that in the future there might be even closer collaboration between the hosiery trade and the Textile Institute. He further added, with no little emphasis, that the Midlands must look to their laurels because the hosiery trade was expanding rapidly and substantially in Lancashire and Yorkshire.

Opportunity was also taken at this meeting to welcome Mr A. Pollard, M.Sc, in his capacity as Head of the Textile Department of the Leicester College of Technology. He was recently appointed to this position in succession to Mr. J. Chamberlain.

The successful designs from all sections of the Competitions were exhibited testifying to the excellence of the work submitted. The complete list of awards and prize winners was printed in the August issue of the *Journal*.

## NOTICES: INSTITUTE MEETINGS

- Tuesday, 4th November—1 30 p m Meeting of the Diplomas Committee at the Institute
- Tuesday, 4th November—2 45 p m Meeting of the Publications Committee at the Institute.
- Wednesday, 19th November—1 0 p m Meeting of the Finance and General Purposes Committee at the Institute.
- Wednesday, 19th November—2 45 p m Meeting of Council at the Institute

### LANCASHIRE SECTION

- Friday, 7th November—Joint Meeting with the Blackburn Textile Society, at the Technical College, Blackburn. Lecture: "Finishing Problems" by A. J. Hall, B Sc (Lond), F I C, F T I

### YORKSHIRE SECTION

- Thursday, 20th November—7 0 p m Lecture "Textile Architecture" by Dr F. C. Toy, D Sc, F Inst P, F T I, Deputy Director of the British Cotton Industry Research Association, at the Midland Hotel, Bradford

### MIDLANDS SECTION

- Saturday, 15th November—2 30 p m Joint Meeting with the Coventry Textile Society. Lecture "Rayon and the Knitter" by L. Rose, A I C, and J. Chamberlain, F T I, at the Technical College, London Road, Hinckley

# OTHER ORGANISATIONS

## *Batley and District Textile Society*

Wednesday, 5th November—7 o p m Lecture " Woollen Rags " by Bernard Hepworth, Esq , at the Technical College.

Monday, 10th November—7 o p m. Inter-Society Debate on " Will Organised buying and selling facilitate the development of research and technology in the Wool Textile Trades? " between Bradford, Dewsbury, Morley and Batley Textile Societies, at the Midland Hotel, Bradford

## *Blackburn Textile Society.*

Friday, 7th November—Joint Meeting with the Textile Institute. Lecture " Finishing Problems " by A J. Hall, B Sc , F I C., F T I , at the Blackburn Textile Society

Friday, 21st November—Lecture " The Principles and Practice of Fibre Analysis " by J M Preston, B Sc., A I C

## *Bradford Textile Society.*

Monday, 10th November—7 o p m. Inter-Society Debate on " Will organised buying and selling facilitate the development of research and technology in the Wool Textile Trade? ", at the Midland Hotel, Bradford, between Batley, Dewsbury, Morley and Bradford Textile Societies

Monday, 24th November—7.0 p.m Lecture " The Selection and Training of Textile Operatives " by H Rostron, B Sc., at the Midland Hotel, Bradford

## *British Association of Managers of Textile Works*

Saturday, 1st November—Open Discussion on " Labour-Saving Devices for Textile Mills " led by Mr. Allan Draper.

## *Coventry Textile Society.*

Saturday, 15th November—Joint Meeting with the Midlands Section of the Textile Institute Lecture " Rayon and the Knitter " by L Rose, A I C , and J Chamberlain, F.T I , at the Technical College, London Road, Hinckley

## *Morley and District Textile Society.*

Monday, 10th November—7 o p m Inter-Society Debate at the Midland Hotel, Bradford

Tuesday, 18th November—Lecture " Scouring and Milling " by C. Archer, Esq

# THE JOURNAL OF THE TEXTILE INSTITUTE

Vol XXXII

DECEMBER 1941

No. 12

## PROCEEDINGS

### Yorkshire Section

#### GALLUP SURVEYS

By Mr HENRY DURANT.

On October 16th an extremely successful meeting of the Yorkshire Section was held at the Midland Hotel, Bradford, under the Chairmanship of Mr Garner, when the lecturer was Mr Henry Durant, Director of the British Institute of Public Opinion. In introducing the lecturer the Chairman pointed out that the British Institute of Public Opinion was affiliated to the now well-known Gallup Survey Organisation of America, and that while polls of public opinion by small sample were best known to those in this country in relation to American political events, their possible applications extended over a much wider field. The B B C for example, had made use of them to ascertain the popularity of programmes, and had it not been for the war a very interesting inquiry was to have been made into the subject of tastes and trend of fashion in Textiles.

In opening his address Mr Durant made brief reference to the history of the development of his organisation, indicating how the war had hindered progress, and then went on to describe how the idea of popular polls had originated in the Gallup organisation. "Dr Gallup first specialised in research in newspaper readership, i.e., into the number of people who read the various features of the newspapers such as leaders and the 'funnies'. Then his mother-in-law became nominated for a second time as candidate for Secretary of State, Iowa, and she wanted to know what were her chances of being re-elected. Dr Gallup undertook to find this out for her and advised her on the strength of the results of his research to stand again, which she did and was re-elected. This gave him the idea that it was possible by means of a small sample to measure the attitudes and the opinions of the public. At first he worked by sending out postcards to a random sample, but as only a small percentage were returned he switched over to interviews, and this is now the means by which we secure our results.

"The interviewer finds the people but he is told what kind of people he is to find. These are classed under six headings or controls — (1) geographical distribution, (2) sex, (3) age, (4) nationality or colour, (5) social grouping, and (6) past voting preference. England is divided into 11 geographical regions, the population of each of which is known, and we allocate our ballots according to the adult population in each district. We reduce the proportion of women that we interview to 35 or 40 per cent because they are not so easy as men to interview. Where, however, their opinions differ from those of the men the results are weighted so that in the final figures reported the women are represented by their true proportion in the total population.

"Our age groups are three — 21-30, 30-49, and 50 and over. In the United States we have to take colour into account whether white or coloured. In England, of course, we do not have that problem to contend with, though Wales

and Scotland are treated as separated geographical units. Another important grouping is that of economic classes. At the present time we employ three. Before the war we had to take the unemployed into consideration, but now the numbers have dwindled to such an extent that there are virtually no unemployed. This leaves three groups. In the lowest group the head of the family has an income of less than £200 per annum, the middle group embraces incomes from £200 to £500 per annum, and the upper group of families are those in which the income is over £500 per annum. These groups are referred to as 'average minus', 'average' and 'average plus,' respectively. This income grouping is based upon the income of the principal wage earner of the family only and not upon the income of the family as a whole.

"Occupational groupings are under seven headings: agricultural workers, industrial workers, civil servants and black-coated workers, personal servants, managerial executive and professional, housewives, and retired and unoccupied. Usually we ask for about 20 interviews from each interviewer, of which, for example, 14 of them shall be from men, perhaps 8 between 21 and 30, 5 between 30 and 50, and the rest over 50. One man shall be wealthy, 4 persons of average income, and 15 average minus. At first the inexperienced interviewer may find himself at the end with the task of finding a wealthy man, aged 21, which is not easy, but, of course, experience soon teaches him how to arrange his interviews.

"There is a surprisingly small amount of fraudulent work among the forms submitted. Actually it is very difficult to sit down and make up all the answers because if that is done either they are all alike or all differ to such an extent that it immediately attracts the attention of the examiner. The forms are carefully checked and although an interviewer may perhaps escape detection in fraudulent work on an odd occasion, it is practically impossible for him to do so twice. The greatest protection is that only a very small fraction of the total number of forms goes into the hands of any one interviewer. Hence, the impact of any one batch of forms is so slight that it is not big enough to affect the ordinary result. The size of the sample taken varies according to the population. In the United States we take a sample of 3,500 but in this country we use about 2,000. In by-elections we take three complete surveys of 500 each and our last results are given on a poll of 500 people. In the Morley (Yorkshire) by-election we not only named the wrong candidate as the winner but we were 6 per cent. out in our forecast. This was hardly our fault because at the last moment one of the candidates made a complete change of policy and our incorrect result was the outcome of stopping our own poll too early. In the by-election at Fulham we were about 1 per cent. wrong, at Lewisham 1.5 per cent., and at the next one only 0.8 per cent. out in our calculations, but nowadays we carry on until the very last moment on the previous day so as to leave the minimum margin of time for such untoward events as the last minute swing which occurred at Morley.

"In the last Presidential Elections in America a State-by-State error of our 48 predictions was only 2½ per cent. In the New York Gubernatorial Election 1938, we were only 0.5 per cent. although in such a close prediction a great deal is due to luck and we cannot hope to maintain such a small margin of error. The Literary Digest in 1932 sent out 10½ million postcards and based their prediction of the Presidential Election on the results obtained from the 2½ million which were returned. As these had been sent, however, to the upper stratum of the population—names derived from the telephone book and automobile lists, for example—they did not get a truly representative cross-section of the voting population, with a result that they proved themselves quite wrong in their calculations: for Roosevelt won the election whilst they had predicted Landon's victory. Their error was no less than 19 per cent. They were not saved from disaster by their enormous sample. Accuracy can be secured only

by the use of a truly representative cross-section. Provided the cross-section is correct the sample may be very small indeed. A great deal depends upon the form and wording of the questions. First we have to satisfy ourselves that the questions selected are interesting to a sufficiently wide section of the public and unbiassed, simple wording must be used. Expert interviewers are then told to try out the questions and to bring back reports as to whether the subject is interesting and the form of question easily understood. This selection of subjects and wording is perhaps the most difficult aspect of the work.

"In England we have more than 400 interviewers and in the United States 1,100 of all ages, and of as good a mixture of types and classes as we can contrive. In the U.S.A. I consider that they have too many students and middle class interviewers, but in this country we are fortunate in that through the Workers' Educational Association, for example, we can get very good interviewers from the 'average minus' group. The interviewers are secured through recommendations, from organisations, or from persons known to us. Most people can be good interviewers without difficulty if they are interested in the work.

"In this country we publish our results in the *News Chronicle*, but we are about to alter that arrangement and hope to publish in the evening papers in the North of England and in Scotland. Some people think that our work is only a poll of *News Chronicle* readers, and it is because of our difficulty in making them believe otherwise that we are trying to make this change, although we have nothing but praise for the way in which the *News Chronicle* has published our results for many years. In the States we publish three times a week in about 110 newspapers."

*Mr Garner* in opening the discussion, urged that greater use should be made of statistical method in the textile trade as a whole, and stated that his own firm had proved it to be of very great value.

"I had had a little previous correspondence with Mr Durant, and my wife and brother have done some interviewing for the Institute, so I have seen some of the inner workings of the scheme, and my own opinion is that it is carried out in a thoroughly scientific manner, and the past records of statistical work are well worth the attention of anyone who requires a public opinion.

"It is surprising to find that interviewers are considered biased, and I should like to know why so many of the results remain unpublished."

*Mr Durant* "With regard to publication of questions—a large amount of work consists of daily surveys for the B.B.C. in which we ask 800 people what they listen to on the wireless, giving them a list of programmes to mark the items they have heard. Already we have done nearly 600,000 surveys for the B.B.C. The results of these are never published. Otherwise we publish 80 per cent of the questions put. Sometimes events move too quickly for publication, by the time they could be in print the need for them would be obsolete.

"As regards the interviewers' bias, we mean by this that the interviewer tends to choose people of his own type for questioning. Also it is often easy unconsciously to push the interviewee a little, press him towards a decision on which he is really rather undecided. We try to choose our interviewers so that the bias will be evenly distributed."

*Mr Royston Millmore* "I have personally taken 2,000 interviews in this town and have every confidence in the impartiality and accuracy of the method. Mr Durant has said that the choice of questions is one of the most difficult aspects of the work, and to give an example, it is no use asking 'Do you regularly attend Church?' A large proportion of people will say that they do attend because they think it is the right thing to say, and in this case the results were as high as 27 per cent. Another thing which I have found fatal is to ask directly the occupation of the interviewee. This never produces the



right answer. It is better to talk to the man, and gradually work round to it during the conversation, in this way your result is much more likely to be right. The form of the questions is vital and it is best to put them in an informal, conversational manner. So far as I can see there is only one objection to this polling, and that is to point out the danger of its being used for a wrong purpose. It could show up the weaknesses prevalent in the public and be used in anti-national propaganda. The English do not take very well to searching questions, and so although I found it easy, very interesting and stimulating, and took many interviews a week, wartime political surveys are not always a pleasant subject to question people about. They are apt to think one a fifth-columnist and so I thought it better to give up the work for the time being, although I shall certainly take it up again after the war."

*Mr Durant.* "Of course, a better wording for 'Do you regularly attend Church?' would be 'Did you go to Church last week?' and would give a much more accurate result. In the United States we used to ask 'Did you go to a University?' and found that such an enormous percentage replied 'Yes,' that we now make them prove that they have actually been, asking how long they were there, what subjects they read, and who was their lecturer. It is important not to ask questions involving prestige.

"The actual wording of the question is not really so vital so long as it is neutral. We asked, for instance, the two questions 'Some people say that since Russia is now fighting Germany there is no longer need to give so much aid to Great Britain. Do you agree or disagree?' and 'Some people say that when Germany defeats Russia she will turn all her strength on England, so it is much more necessary to give aid to Great Britain. Do you agree or disagree?' The difference in results was negligible, as the answers actually varied between 72 per cent and 73 per cent in favour of aid to Britain."

*Mr Masters.* "To give a textile application, a useful one would be with regard to the coupon system. How was it originated, through the opinion of wholesalers in London, or was it based upon the German system which has been established for some years, or was it based upon what it was thought people ought to have or what they wanted? Are the public getting what they want or what they ought to have?"

*Mr Durant.* "In this country, it is difficult to understand why the Government seldom, if ever, ascertains the public's attitude before making some such move. The Board of Trade is now using a survey to investigate the coupon situation, but it is only since difficulties arose that surveys have been taken. They are trying to find out what the people really need and to modify the system accordingly. The United States has allocated a yearly sum of 200,000 dollars for sounding public opinion, and it is a pity that this Government does not do the same. In the U.S.A. Dr Gallup undertook to find out why the enlistment for the American Navy had fallen, and alterations made in publicity after our research had been carried out resulted in an improvement of over 300 per cent."

*Mr Hardy.* "You mentioned with regard to your interviewers that you employ a number of people who are selected by the Workers Education Association. Are they part-time workers? (Mr Durant, "Yes, they are part-time.") Then do they spend a fair amount of time searching in working men's clubs, and at what time of day do they take the interviews? Because the big proportion of workers are in the mills from 7 a.m. to 5-15 p.m. and they would miss the bulk of the workers during the daytime. In the treatment of economic and geographical groupings I can see a difficulty, for example, in the great difference between the people in Batley, Morley and Ossett although they are all in the same geographical area, and the question of part-time interviewers does not seem entirely satisfactory. A few full-time interviewers might make for more accuracy."

*Mr Durant* "For election forecasts we have a full-time staff for a week. We survey at the mills during the lunch hour or any suitable break, and do a certain number of ballots in the evening, continuing until the last moment on the evening previous to the polling day so as to take care of political bombshells"

*A member of the audience* "Do you undertake commercial work?"

*Mr Durant* "Plenty in America, but we have not done any in this country. If the results are published our name must be suppressed, since publication of that is reserved exclusively for our newspaper work. Although we do not seek it we are interested to do it and are willing to help as much as possible. If you want any work of this sort done, have it done by someone whom you can trust. There are a number of extremely reputable agencies, but be careful to use one of them."

*Mr Halliday* "Do the interviewers record the comments, and is any use made of them or not?"

*Mr Durant* "We get more satisfactory answers to the type of question which requires the answer 'I am satisfied' or 'I am dissatisfied,' than to a question which involves a choice of graded alternatives. In addition we believe that having to choose between two hard and fast alternatives is more realistic. In everyday life it is usually a case of 'Yes' or 'No,' without any middle position in which we can take refuge. Faced with a variety of statements people will veer from extremes and choose a comfortable middle course which will not commit them to a decided statement. We do record comments, we are going to write up our results more fully, using the comments as much as possible. This, we hope, will make the results more interesting. We hope to distribute this broadsheet once a month."

*Mr Masters* "Do you consider the surveys taken by the Board of Trade to be accurate? Have they discovered the shortage of the cheaper types of cloth in the shops? Can they estimate public opinion as does the Gallup Survey?"

*Mr Durant* "Mr Francis Meynell is in charge of the Board of Trade research and their results can be trusted. Mr Moss, our statistical manager, is in charge of the surveys for the Ministry of Information, and their results can be relied upon."

*Mr Kohner* "Do you select interviewers from among the local people, and do you work in Eire?"

*Mr Durant* "Yes, we use local interviewers. Their travelling expenses are less and they know the district and the whereabouts of the likely people. We have tried to work in Eire but we cannot do political work there and there is nothing else of great interest."

Mr Halliday proposed a vote of thanks to Mr Durant which was seconded by Mr Kohner, whereupon the Chairman, Mr Garner, drew the meeting to a close commenting that the lecture had been one of the most interesting the Yorkshire Section had had for many years.

## Obituary

### Harry Nisbet, F.T.I.

The sudden death of Harry Nisbet, F.T.I., at the age of 72 years, has deprived the Institute of one of its active members who was not only one of the founders of the Institute in 1910 but also a prominent councillor who gave invaluable service to the cause of textile technology.

He was a native of Preston, but at the early age of 13, he, together with the family, moved to Bolton where he was apprenticed to textile designing with Messrs Barlow and Jones, Ltd, and remained with the firm as a jacquard cloth designer for fourteen years. By dint of patient, energetic and persistent

application he acquired a remarkably sound knowledge of design, cloth structure and weaving, with the result that in 1892 he became an assistant to the late John Crompton in weaving instruction at the Bolton Technical College. Four years later he succeeded Mr Crompton as the Weaving Master at the College and successfully carried out these duties for 21 years. His excellent contribution to the progress of textile education is reflected by the warm praise and success of the many students who passed through his hands during the 25 years that he was engaged in the teaching profession.

A firm believer in the axiom that knowledge is the successful application of education, experience and ability acquired, in 1917 he transferred his energy again to the industrial field and held the position as head of the research and testing laboratories of a textile firm.

In his desire to enrich the industry he was a pioneer of textile education of outstanding merit, the author of many articles and books on designing, weaving and other textile machines and operations, and a well-known textile technologist and consultant.

His unstinting support was always available to the Institute, of which he was a member of the Council for many years, and up to the time of his death he attended the meetings regularly. His wide experience was available as a member of the following Committees—Publications, Library, Textile and Designs, Lancashire Section, and as an Institute representative to the Federation of Textile Societies. He was also a member of the Textile Teachers' Association (Lancs Section).

In addition to being a foundation member of the Institute he was admitted as a Fellow in 1926 and as some reward for his services he was awarded the Institute Medal in connection with its coming-of-age celebrations in 1931.

Throughout the whole of his working life he was willing and anxious to share his experience and knowledge with those interested in textiles and his help and wise counsel will be seriously missed.

H BROMLEY

## Review

**"Intermediate Domestic Science, Part II, Textiles in the Home".** By W. Munn Rankin and E. M. Hildreth. Allman & Son Ltd, 73, Minories, E.C.3. Price 3/-.

Messrs Rankin and Hildreth have prepared two volumes on "Intermediate Domestic Science," the first dealing with Foods and Dietetics and the second with Textiles in the Home. They are primarily intended for students in Domestic Science Colleges, but Volume II will be of interest to Textile Students. It contains a general description of textile raw materials in the first 32 pages and this section is illustrated with photomicrographs of the various fibres. The second part of the volume covers 80 pages and consists of notes and routine experiments on fibres and fabrics, dyes and dyeing, soap and laundry materials, stains on fabrics and finally, bleaching. Many of the experiments could, with advantage, be applied in a testing course for textile students. The volume is full of scientific and technical information relating to textiles.

J R

## Examinations in 1942

Applicants for Associateship who have been referred to the Preliminary Examination should note that this Examination will be held in Manchester on Wednesday, 11th March, 1942. The Examination in General Textile Technology will take place on Wednesday, 20th May, 1942, at convenient centres which will be announced later.

Notification of entry should be given to the Acting Secretary not later than one calendar month before the date of the Examination.

# THE Journal of the Textile Institute.

VOL. XXXII—1941

## PROCEEDINGS—NAME INDEX

In this Index (R) indicates that the matter is the subject of a Review.

	PAGE		PAGE
<b>B</b>		<b>R</b>	
Bromley, H. Obituary Notice of Mr. H. Nisbet, F.T.I.	P111	Rankin, W. Munn, and Hildreth, E. M. "Inter- mediate Domestic Science, Part II, Textiles in the Home" (R)	P112
<b>D</b>		Roston, H. Selection and Training of Operatives in the Textile Industry	P50
Draper, A. Twistless and Low Twisted Yarns	P53	<b>S</b>	
Durant, H. Gallup Surveys	P107	Smith, R. J. "Plastics in Industry" (R)	P14
<b>H</b>		"Textile Finishing in War-time"	P69
Hildreth, E. M. See Rankin W. Munn	P112	<b>T</b>	
<b>M</b>		Thompson, G. H. Presidential Address	P34
Mark, H. "Physical Chemistry of High Polymeric Systems" (R)	P93	Thompson, L. Review of "Mercerising," by J. I. Marsh	P89
Mark, H., and Whitby, G. S. "Collected Papers of Wallace Hume Carothers," (R)	P93	Tuckett, R. H. Reviews of "Physical Chemistry of High Polymeric Systems" and "Collected Papers of Wallace Hume Carothers"	P93
Marsh, J. I. "Mercerising" (R)	P89	<b>U</b>	
<b>P</b>		Ullmann, G. The Spinning of Dyed and Bleached Yarns	P1
Pickering, A. J. "Cradle and Home of the Hosiery Trade"	P21	Ungerson, L. Industrial Psychology	P56
du Plessis, A. Foster. Wool—The Warp and Woof of the British Commonwealth of Nations	P82	<b>W</b>	
		Whitby, G. S. see Mark, H.	P93
		Wood, F. C. Reports on the Progress of Applied Chemistry, Vol. 25, 1940 (R)	P89



# PROCEEDINGS—SUBJECT INDEX

3

	PAGE		PAGE
<b>A</b>		<b>O</b>	
Additions to the Library	P94	Obituary—	
Associateships, Award	P13, P38, P44, P68, P92, P95, P113	John Crompton, O B E , M Sc (Tech), F T I	P45
		James F Copley	P46
		Edwin H Marble	P47
		H Nisbet, F T I	P111
<b>C</b>		<b>P</b>	
Collected Papers of Wallace Hume Carothers		" Physical Chemistry of High Polymeric Svstems	
H Mark and G S Whitby (R)	P93	H Mark (R)	P93
Council's Annual Report for 1940	P26	Presidential Address G H Thompson	P34
<b>E</b>		<b>R</b>	
Effect of the War on Textiles London Section		" Rayolanda "	P59
Luncheon Meeting, 1/5/41	P48	Reviews—	
Employment Register	P14, P24, P39, P45, P68	" Plastics in Industry " Plastes	P14
Examination in Analysis and Testing of Materials,		Ravon and Silk Directory and Buyers' Guide of	
1941 Question Paper	P98	Great Britain, 1940-41	P21
Examination in General Textile Technology, 1941		" Cradle and Home of the Hosiery Trade " A J	
Report of Examiners and Examination		Pickering	P21
Papers	P96	Report on the Progress of Applied Chemistry,	
Examination Results, 1941	P68	Vol 25, 1940	P89
<b>F</b>		" Mercerising " J T Marsh	P89
Fellowships, Awards	P13, P38, P44, P95	Royal Society of Arts Results of Competition for	
		Students of Textile Design, 1941	P81
<b>G</b>		<b>S</b>	
Gallup Surveys H Durant	P107	Scottish Section	P37
<b>H</b>		Selection and Training of Operatives in the Textile	
Honorary Fellowship Award Mr Fernando		Industry H Rostron	P50
Casablanças	P63	Spinning of Dyed and Bleached Yarns G Ullmann	P1
<b>I</b>		Summer Meeting, 1941	P61
Industrial Psychology L Ungerson	P56	<b>T</b>	
Institute Balance Sheet and Accounts for 1940	P29	Textile Finishing in War-time R J Smith	P69
Institute Membership	P13, P24, P39, P44, P68, P92, P95, P113	Textile Institute Competition Awards, 1941	P79
Institute Service Medal Awards	P17, P19	Textile Institute Medal Award, Mr W W L	
Intermediate Domestic Science, Part II Textiles		Lishman	P65
in the Home W Munn Rankin and E M		Twistless and Low Twisted Yarns A Draper	P53
Hildreth (R)	P112	<b>W</b>	
Irish Section	P21, P36	Wool, The Warp and Woof of the British Common-	
<b>L</b>		wealth of Nations A Foster du Plessis	P82
Lancashire Section	P12, P36, P50, P78, P102	<b>Y</b>	
London Section	P36, P48	Yorkshire Section	P18, P38, P56, P92, P100, P107
<b>M</b>			
Midlands Section	P37, P91, P104		
Notes and Announcements	P12, P17, P25, P61, P79, P95		



THE JOURNAL  
*of the*  
TEXTILE INSTITUTE

VOL. XXXII—1941



TRANSACTIONS AND INDEX





JANUARY 1941

II

# THE JOURNAL OF THE TEXTILE INSTITUTE

## TRANSACTIONS

### 1—THE FLUIDITY OF SILK SOLUTIONS

#### Part I. MEASUREMENT

By CHARLES HERBERT GARRETT, M A , A.Inst.P., and

FREDERICK OLIVER HOWITT, Ph D , F.I.C., F T.I.

(The British Cotton Industry Research Association · Silk Section)

(Copyright by the Textile Institute)

#### I. Introduction and Summary.

The determination of the fluidity of cellulosic material (Chibbens and co-workers<sup>1, 2</sup>) in a cuprammonium solvent has proved of great value in the assessment of chemical degradation of cotton and rayon materials. The success attending the application of this method had indicated the need for an analogous test applicable to silk but, up to the present time, only one such method for the differentiation of chemical and mechanical damage in silk (in this paper, "silk" means degummed silk) has been published<sup>3, 4, 5</sup>. The method depends on the use of concentrated solutions of zinc chloride as a solvent for silk, and for reasons given in this paper it is not regarded as very satisfactory. It is therefore considered that all reagents known to dissolve silk should be examined with regard to their applicability to a fluidity test for silk. Of the reagents examined, one appears to be of outstanding merit, namely, cupri-ethylenediamine solution. This, however, suffers from the disadvantage of degrading the dissolved silk at a significant rate, but fortunately the degradation is almost eliminated by neutralisation of the cupri-ethylenediamine complex after dissolution of the silk. An interesting feature of this neutralisation is that, whilst the solutions of fibroin thus obtained are quite stable and suitable for viscometric examination, neutralisation of cupri-ethylenediamine reagent gives a solution incapable of dissolving silk.

The method finally adopted is that of dissolving silk in a reagent containing 8 per cent of ethylenediamine and 6 per cent of cupric hydroxide to give a solution 10 per cent (weight/volume) in silk, calculated as dry weight; this solution is neutralised with an equal volume of acetic acid (to

give a solution 5 per cent. in silk) and the fluidity is determined. The method of preparing and standardising the solvent is described. During the early work with this solvent, the viscometer devised by the British Cotton Industry Research Association for work on cellulose was used. It was found advantageous to replace this instrument by a U-tube type and a detailed specification of this viscometer is given. The instrument is readily calibrated by the use of reference standards, e.g. pure phenylethyl alcohol.

Measured by the method described in this paper, the fluidity of a solution of untendered silk is approximately 4 reciprocal poises, whilst for silk chemically tendered to an extent corresponding with almost complete loss of strength, the fluidity is approximately 50. Expressed alternatively in viscosity units, the range is from about 25 to 2 centipoises. As a result of this wide (12-fold) range, a sensitive measure of chemical tendering is obtained that does not require very great accuracy in the measurement of the rate of flow. Examples of the application of the test and typical data afforded are given in Part II of this work (p. 113).

## II. Selection of Solvent and Conditions of Measurement.

The following are considered to be the characteristics of a suitable solvent:

- (a) It is readily and cheaply prepared.
- (b) It is sufficiently stable for routine use.
- (c) It causes no appreciable degradation of silk during the period necessary for the preparation of the solution and the measurement of its fluidity.

Unequivocal evidence of a degrading action of the solvent is provided when the fluidity of the silk solution increases rapidly with time in repeat measurements on the same solution. No change, or only a slight change, of fluidity in repeated viscometer runnings is not, however, a sufficient criterion of compliance with the requirement (c), since if a large degrading effect occurs during the preparation of the solution, the subsequent drift in fluidity must in any case be relatively slow. Under these conditions, the measured fluidity will be determined partly by the degrading action of the solvent, and partly by the original quality of the silk. If the techniques of dissolution and measurement are strictly standardised, it might be assumed that the degrading effect of the solvent is in some sense constant, and that the fluidity measurement is therefore of diagnostic value as a test of the silk quality. It is clear, however, that the greater the degrading action of the solvent, the less sensitive must the test become as an index of silk quality.

A concentrated aqueous solution of zinc chloride has been recommended as the solvent for measuring the flow properties of silk solutions (Trotman and Bell<sup>3</sup>, Trotman<sup>4</sup>). In the proposed method, the concentration of silk is 2.5 per cent., and dissolution is effected by incubation at 37° C. for six hours. Although the rate of flow of solutions prepared in this way only changes slowly, it is probable that considerable degradation of the silk occurs under the conditions necessary to effect complete solution in a zinc chloride solvent. This is suggested by the results obtained by Tweedie<sup>5</sup> in a study of the relation between the tensile strength of chemically tendered

silk and the fluidity of its solution in aqueous zinc chloride. The results show that the fluidity determined in this way provides only a very insensitive index of loss in strength resulting from the various types of chemical tendering studied by Tweedie. It may also be noted that the relative viscosity of a 2.5 per cent solution of untendered silk measured by Trotman's method is in the neighbourhood of 2. Since silk almost certainly belongs to the group of natural polymers of high molecular weight, this low value also suggests that considerable degradation is caused by the dissolution process

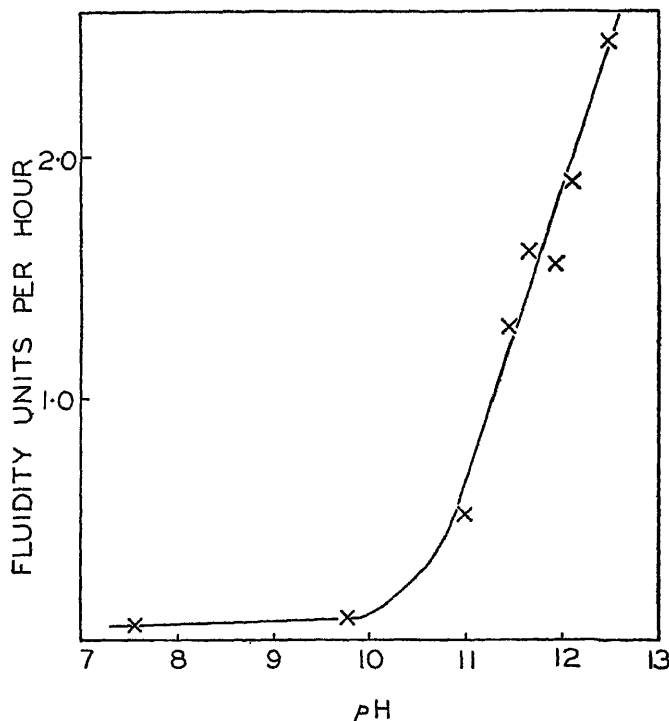


Fig 1 Curve showing the rate of change of fluidity on standing of a 5 per cent. solution of silk (initial fluidity approximately 12.5) at different values of pH

The known solvents for silk fall into one of three categories, namely,

- (1) Concentrated aqueous solutions of the halides, nitrates, and thiocyanates of certain metals, e.g., zinc, calcium, and lithium.
- (2) Strong acids and bases of certain concentrations
- (3) Basic solutions containing complex derivatives of copper or nickel.

Many solvents in these three classes have been examined with regard to their suitability for use in rate of flow measurements. Of those in the first class, zinc chloride was found to be the best solvent, in agreement with the conclusions of Trotman and Bell. The strong acids and bases were found to exert much too rapid a degrading action for the purpose in view. The following complex basic systems were then examined as possible silk solvents:

- (a) Solutions of nickel hydroxide in (i) aqueous ammonia (Richardson's reagent) and (ii) aqueous ethylenediamine.

(b) Suspensions of freshly precipitated cupric hydroxide in dilute sodium hydroxide solution

(c) Solutions of copper hydroxide in (i) aqueous ammonia, (ii) alkali-glycerol (Loewe's reagent), (iii) aqueous ethylenediamine ("cupri-ethylenediamine") and (iv) glycerol-cupri-ethylenediamine

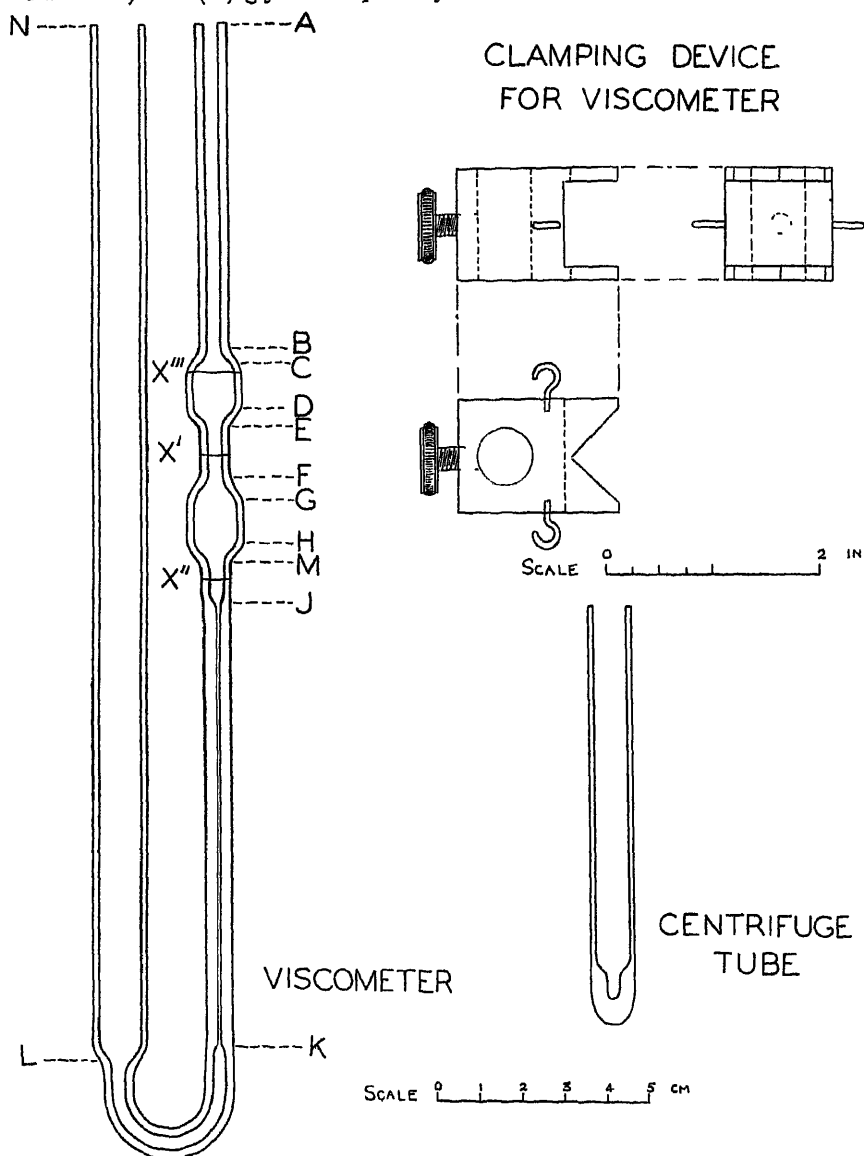


Fig 2

Of these, cupri-ethylenediamine was much the most promising, suitable solutions of this complex dissolving up to 12 per cent of silk rapidly in the cold to yield highly viscous solutions (cf. Takamatsu *et al*<sup>6</sup>). The fluidity of such solutions rose fairly rapidly with time of standing, indicating a pronounced degrading action of the solvent, and this is not unexpected in view

of the fact that cupri-ethylenediamine is a strong base, comparable in this respect with the hydroxides of the alkali metals. It was observed, however, that after dissolution of the silk, the base could be neutralised by acetic acid without precipitation of the protein and that the fluidity of the resulting solution changed only slowly with time (1 per cent. per hour or less). Since the dissolution of the silk and subsequent neutralisation of the solution could be carried out very rapidly, the alkaline degradation of the silk by the solvent could be reduced to a minimum, and the conditions thus appeared very favourable for the preparation of silk solutions for measurements of rate of flow.

The composition of an aqueous ethylenediamine solution saturated with cupric hydroxide corresponds approximately with the formula  $\text{CuEn}_2(\text{OH})_2$ , (where  $\text{En}=\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ ) for the complex copper base, although the solution contains slightly more copper than is required by this formula. Such saturated, or nearly saturated, solutions are, however, somewhat unstable and the solvent used in the present work is not quite saturated with respect to copper hydroxide. Its composition is:

	Gm per 100 c c	Molarity
Ethylenediamine	8.0	1.335
Cupric hydroxide	6.0	0.615

If an equal volume of 1.33*N*-acetic acid is added to this solution, its *pH* is reduced from its initially high value (approximately 12.8) to the neighbourhood of the neutral point (*pH* 6.9–7.0), and the liquid loses its solvent power for silk. A similar neutralisation of a 10 per cent. solution of silk in the alkaline reagent can, however, be carried out without precipitation of the protein, the resulting solution is also neutral in reaction, is stable, and its fluidity changes but slowly. Acid in excess of an equal volume of 1.33*N*-acetic acid produces separation of the silk as a colloidal aggregate (suspension form) and, when this amount of acid is used, care must be taken to avoid local high concentration of acid during its addition. On this account, it was found advisable to neutralise with an equal volume of a slightly less concentrated acid, namely, 1.25*N*-acetic acid. This gives a slightly alkaline (*pH* approximately 9) solution which, however, is still sufficiently stable for the measurement of fluidity, as is shown by the curve of *pH* plotted against rate of change of fluidity (Fig. 1). The concentration of silk in the solution is reduced from 10 per cent. to 5 per cent. by the addition of the acid and this is the standard concentration employed. The measurement of fluidity is made in a U-tube viscometer with a small working volume (3 c.c.) in order to keep the weight of silk required for the test as small as possible.

The rest of the paper is devoted to a detailed description of the apparatus, the method of preparing the solvent, and the technique for dissolving the silk and for measuring the fluidity of its solution. The practical utility of the method for assessing the quality of silk, which is the most important criterion of its value, is discussed in the succeeding paper.

### III. Viscometer.

*Specification of viscometer*—As indicated above, it was found that The British Cotton Industry Research Association instrument used for cellulose could be replaced with advantage by a U-tube type of viscometer of small

capacity. The construction of the model finally adopted is shown in Fig. 2. The dimensions of the viscometer are as follows:—

Internal diameter of capillary JK .. .. .	0.088 ± 0.001 cm.
External diameter of capillary JK . . . . .	0.6 ± 0.2 cm
Length of capillary JK . . . . .	10.0 ± 0.2 cm
Internal diameter of cylindrical parts of the bulbs BE and FM . . . . .	1.0 ± 0.02 cm
Length of tube EF . . . . .	1.5 ± 0.3 cm.
Length of tube MJ .. ... . .	1.0 ± 0.2 cm.
Length of tube KL . . . . .	about 7 cm.
Internal diameter of tubes AB, EF, MJ, and KL	0.325 ± 0.025 cm
Length of tube AB . . . . .	7.5 ± 0.5 cm
Length of tube LN . . . . .	about 24 cm
Internal diameter of tube LN . . . . .	1.0 ± 0.05 cm
Volume of each bulb (BE and FM) .. . . .	1.2 ± 0.05 c.c.
Volume between etched rings X' and X''	1.3 ± 0.05 c.c.
Clearance between tube NL and bulbs	about 1 cm
Over-all length of viscometer	about 26 cm

Whilst the upper bulb is not used as a standardised unit of the viscometer, the use of two bulbs results in a correction of the draining error in the lower bulb and also affords a choice of the more exact volume during construction of the viscometer. The mark X''' indicates the level to which the silk solution is drawn up by applying suction at A. For 3.00 c.c. of solution, this corresponds with a level in the other limb very near the bottom of the wider tube NL.

The viscometer requires a 3.00 c.c. pipette for filling purposes; this pipette must be calibrated and used with maximum accuracy.

The viscometer is held in position in the bath by clamping the wide-tube arm to two V-shaped blocks by means of rubber bands. The two blocks fit on a rod which is maintained in a vertical position by suitable stands and clamps, the rod is fitted with a plumb-line and, at the lower end, a rubber bung which rests on the bottom of the tank. Suitable dimensions for the blocks are given in Fig. 2. With this arrangement, three or four viscometers can be fitted into a glass tank approximately 9½" by 11" by 16½" deep (these are the dimensions of one type of glass accumulator cell).

*Calibration of viscometer.* The method of calibrating the viscometer consists in measuring the time of flow at 20° C (*t*) of a liquid of known fluidity (*F*) and density (*d*), flowing sufficiently slowly to keep the kinetic energy correction low, this gives the viscometer constant *C* in kinematic units (reciprocal stokes). Since the results are to be expressed in dynamic units (reciprocal poises) and since the viscometer is only intended for use with silk solutions of constant composition (3 per cent. Cu(OH)<sub>2</sub> - 4 per cent. En - 5 per cent. silk), the density can be included in the constant term, and it is assigned the value 1.039 at 20° C. A constant (*C'*) can then be calculated, expressed in seconds per poise and applicable only to silk solutions, which facilitates subsequent calculations. An actual example of the calibration is as follows:—

## Viscometer S1

Time of flow of phenylethyl alcohol ( $d^{20}_w$  1.019,  $\eta^{20}$  7.01,  
 $dF^{20}$  7.14) .. .. = 126.3 seconds

Viscometer constant (in seconds per stokes) =  $7.14 \times 126.3 = 901.8 (C)$

Viscometer constant (in seconds per poise) for cupri-  
 ethylenediamine solutions of silk . . . =  $\frac{901.8}{1.039}$   
 = 868.2 ( $C'$ )

The fluidity  $F$  of a silk solution is then given by the simple expression

$$F = C'/t = 868.2/t$$

The kinetic energy correction is very low within the fluidity range of interest. It is made by subtracting from the observed time ( $t$ ) a quantity  $k/t$  in which  $k$  is an instrumental constant. The value of this constant can be calculated approximately from the expression  $k = VC/8\pi l$  where  $V$  is the efflux volume and  $l$  the capillary length. With the dimensions specified, the value of  $k$  thus lies between 4 and 5, when  $C$  has a value of about 900. This means that at a fluidity of 40, the kinetic energy correction is about 1 per cent, whilst at fluidities of 10 and below it does not exceed 0.1 per cent. Since silk solutions of fluidities greater than 40 will rarely be encountered, it is clear that the correction is generally negligible. The low value of the correction constant  $k$  can be checked experimentally by observations on liquids of known high fluidities.

## IV. Cupri-ethylenediamine Solvent.

The solvent is prepared by dissolving cupric hydroxide in ethylenediamine solution. The cupric hydroxide preparation used should be of good quality, e.g., the  $\text{Cu}(\text{OH})_2$  and water contents should total 99–100 per cent. Commercial preparations of cupric hydroxide frequently contain anions such as sulphate or nitrate of which the sulphate is the more common. This sulphate is present in a water-insoluble form (the so-called basic sulphate) and it reacts with ethylenediamine to give cupri-ethylenediamine sulphate  $(\text{CuEn}_2)\text{SO}_4$ . Formation of the sulphate is preferential to that of the hydroxide of the base and, consequently, when aqueous ethylenediamine is shaken with excess of a cupric hydroxide preparation that contains sulphate, all the sulphate present is taken into solution as cupri-ethylenediamine sulphate. The presence of sulphate (or nitrate, etc.) in the cupri-ethylenediamine reagent decreases its basic property and this leads to an acid reaction (and consequently precipitation of fibron) when the standard amount of acetic acid is added to the unneutralised solution of silk in the cupri-ethylenediamine reagent. A suitable preparation of cupric hydroxide should therefore be substantially free from sulphate, chloride, nitrate, and, for reasons converse to those applying to sulphate, from caustic alkali. In addition to these qualitative tests, analytical control of the hydroxide can be carried out by

(a) determination of loss of water at  $110^\circ \text{C}.$ ,

(b) dissolution of a weighed amount in excess of standard hydrochloric acid and back-titration with standard alkali, and

(c) dissolution of a weighed amount in standard hydrochloric acid and iodometric determination of copper



Ethylenediamine is supplied\* in the form of a concentrated solution (approximately 70 per cent weight/volume) in water. This solution is diluted to a strength of 8.0 ( $\pm 0.05$ ) per cent. with distilled water and checked by titration to pH 4.5 (B.D.H. 4.5 indicator) with standard hydrochloric acid solution. The true amino content can be conveniently determined by the Van Slyke micro-method for amino-nitrogen. The cupri-ethylenediamine reagent is prepared by shaking about 70 gm. of the cupric hydroxide with 1 litre of the 8 per cent. (weight/volume) ethylenediamine solution for approximately 1 hour and centrifuging the mixture or filtering it through an asbestos pad to remove the small insoluble residue. The filtrate can be examined by the following procedure†:—

Five c.c. of the filtrate are added to 25 c.c. of *N*-hydrochloric acid. Twenty c.c. of 10 per cent. potassium iodide are added to the mixture and the liberated iodine is titrated with 0.1*N*-sodium thiosulphate and starch as indicator, this gives the copper content. When the titration is complete, about five drops of excess thiosulphate solution and two drops of B.D.H. 4.5 indicator are added to the contents of the flask (i.e., without filtration), and the mixture is titrated with *N*-sodium hydroxide. When allowance is made for the *N*-hydrochloric acid taken up by the copper, 25 c.c. of *N*-acid less the back titre gives the equivalent amount of ethylenediamine.

The concentration of  $\text{Cu}(\text{OH})_2$  in the solution will be found to be 6.1-6.3 per cent., the content corresponding with  $(\text{CuEn}_2)(\text{OH})_2$  is 6.4 per cent. The calculated volume of 8.0 per cent. ethylenediamine solution is then added to give concentrations of  $\text{Cu}(\text{OH})_2$  and ethylenediamine of 6.0 per cent. and 8.0 per cent. (weight/volume), respectively. No significant divergence from these concentrations is desirable, the tolerance allowable is 5.95-6.05 and 7.9-8.1 per cent. (weight/volume), respectively, but values of 5.95 per cent. for the concentration of cupric hydroxide and 8.10 per cent. for that of ethylenediamine in one solution should be avoided if possible.

The standardised reagent may be kept for several months if stored at normal temperature in a brown-glass container and not exposed to light; storage in white-glass containers exposed to daylight causes decomposition with deposition of cuprous oxide.

The density of the reagent is 1.062 at 20° C. and its fluidity, after addition of an equal volume of 1.25*N*-acetic acid, is 75 reciprocal poises. The density of the neutralised reagent containing 5 per cent. of fibroin is 1.039 gm. per c.c.

#### V. Technique of the Method

The silk to be tested is conditioned at 65 per cent. relative humidity and 65° F. and 193 mg. is introduced into a vessel of about 10 c.c. capacity, small flat-bottomed specimen tubes,  $2\frac{1}{4}$  cm. in diameter and  $3\frac{1}{4}$  cm. deep, are very suitable. By means of a pipette specially calibrated for the purpose (time of delivery 10-20 seconds) 1.75 c.c. of the cupri-ethylenediamine reagent are run into the tube and the mixture is stirred vigorously with a small glass rod for exactly 3 minutes and then the stirring is continued while 1.75 c.c. of 1.25*N*-acetic acid is slowly run in. The 3-minute period, which is generally sufficient for complete dissolution to be effected, is timed with a stop-watch and applies from the commencement of dissolution to the beginning of neutralisation. The acid is delivered from a micro-burette and the jet of the burette is constricted so that with the tap fully turned on the

\* By General Chemical & Metallurgical Co., London.

† Devised by Mr. D. Coleman, B.Sc.

time of delivery of 1.75 c c is approximately one minute. Local concentration of acid during the neutralisation must be avoided and hence vigorous and careful stirring during neutralisation is necessary. A small glass propeller driven by an electric motor (e.g., from a domestic type of electric fan) can be used with advantage for this stirring. The neutralised solution is then transferred to a small glass centrifuge tube at the base of which is a well (shown in Fig. 2) so that on centrifuging the small amount of insoluble matter often present in the silk solution is packed into a compact mass which will not be drawn into the pipette. The solution is then centrifuged for 5 minutes at 1000-1200 r p m; for this purpose, a two-bucket water-turbine centrifuge is suitable. By means of a specially calibrated pipette, 3.00 c c of the solution are withdrawn from the centrifuge tube (care being taken not to disturb any residue in the well of the centrifuge tube) and transferred to the viscometer, the solution being allowed to trickle down the inside of the wide tube of the viscometer so that no air bubbles are produced in the capillary. The viscometer is kept in a water-bath fitted with a thermostat to maintain a steady temperature of 20° C and a period of 10 minutes is allowed for the temperature of the silk solution to attain this temperature. The time of flow is then determined by drawing the liquid up to the mark X''' in the upper bulb by applying suction at A (an ordinary filter pump is suitable for this purpose) and recording the time for the level to fall from X' to X'' with a stop-watch recording one-tenth seconds. Several determinations are made and the readings should agree within  $\pm 0.2$  second, the mean of all the readings is taken for the purpose of calculation. The correction for kinetic energy can be neglected excepting for relatively high fluidities

#### Examples—

##### (a) Normal, degummed silk waste

Viscometer S<sub>1</sub> C' = 868 k = 4.5

Time of flow = 66.2, 66.3, 66.2, 66.4 seconds

Mean = 66.3 seconds

$$F = 868 / 66.3 = 13.1$$

$$k/t = 4.5 / 66.3 = 0.07 \text{ and is negligible}$$

Viscometer S<sub>1</sub> C' = 893 k = 4.0

Time of flow = 69.2, 69.4, 69.2, 69.0, 69.2 seconds

Mean = 69.2 seconds

$$F = 893 / 69.2 = 12.9$$

##### (b) Tendered silk yarn

Viscometer S<sub>2</sub> C' = 774 k = 4.0

Time of flow = 18.45, 18.5, 18.5, 18.3, 18.5, 18.4 seconds

Mean = 18.4 seconds

$$F = \frac{774}{18.4 - \frac{4.0}{18.4}} = \frac{774}{18.4 - 0.22} = \frac{774}{18.2} = 42.5$$

Viscometer S<sub>4</sub> C' = 893 k = 4.0

Time of flow = 20.9, 21.1, 21.0, 20.9, 21.1, 20.9 seconds

Mean = 21.0 seconds

$$F = \frac{893}{21.0 - \frac{4.0}{21.0}} = \frac{893}{21.0 - 0.2} = \frac{893}{20.8} = 42.9$$

The viscometer is cleaned after a fluidity determination by sucking through, successively, dilute caustic soda, water, and acetone and finally drying with a current of dry, clean air

#### VI. Effect of Temperature

The determination of silk fluidity, as described above, necessitates the use of a thermostat in order to ensure a steady temperature of 20° C. Some observations were made on the effect of small variations in temperature on fluidity with the object of determining the permissible latitude in temperature in order to obtain a definite degree of accuracy. The viscometer was filled with a silk solution of fluidity approximately 13, immersed in a bath the temperature of which was adjusted consecutively to 19.0, 19.5, 20.0, 20.5, and 21° C., and the time of flow at each of these temperatures was observed. The series of readings was then repeated for the same temperatures in decreasing sequence, i.e., from 21.0 to 19.0° C., the experiment being arranged so that each series of readings occupied the same interval of time (1½ hours). The two series of readings gave, on graphing, two non-parallel straight lines, one representing the sum the other the difference of the effect of temperature and the small but relatively significant effect of time alone, these two effects could therefore be calculated from the data obtained. The whole experiment was repeated on a silk of fluidity approximately 7, and the results thus given were—

$$F=13$$

Temperature coefficient = 0.39 c g s units (2.9 per cent) per 1° C

Time coefficient = 0.09 c g s units per hour.

$$F=7$$

Temperature coefficient = 0.285 c g s units (3.48 per cent.) per 1° C

Time coefficient = 0.10 c g s units per hour.

Temperature coefficient of solvent ( $F=75$ ) = 2.8 per cent per 1° C.

Thus a silk solution, prepared in the normal manner, of initial fluidity 7.0 at 20.0° C. will give a value of 7.1 if kept for 1 hour at 20° C. but one of 7.4 if kept for 1 hour during which the temperature increases to 21° C. It is found that the time coefficient appears to decrease with time, solutions of fluidity 10-30 at 20° C. gave values higher by 0.3-0.5 units when kept overnight (at room temperature) and re-examined at 20° C.

A strict control of temperature is therefore unnecessary for routine examination of silk fluidity, a temperature range of 19-21° C. giving results of sufficient accuracy for most purposes, this means that by using a large water-bath thermostatic control need not be used, with little resulting inconvenience.

#### VII. Effect of Concentration of Fibroin

The relation between the fluidity and concentration of silk solution has been examined (a) for an untendered silk of fluidity 7.8 in 5 per cent. solution and (b) for a tendered silk of fluidity 21.1 in 5 per cent. solution. The results are given in Table I.

Several empirical equations have been set up to represent the viscosity/concentration relation for colloidal solutions over a wide concentration range and one of the most satisfactory of these is that due to Baker<sup>7</sup>

$$\eta_r = (1 + aC)^b \quad \dots \quad (1)$$

In this equation,  $\eta_r$  is the relative viscosity of the solution (fluidity of solvent/fluidity of solution) and  $C$  is its concentration;  $a$  and  $k$  are empirical constants. Experimental data can often be fitted satisfactorily to an equation of this form, but the exponent  $k$  is so high that a considerable variation in its value is possible without seriously affecting the accuracy of the fitting. Thus, the following two equations have both been employed successfully to represent the viscosity/concentration relation for solutions of various natural polymers of high molecular weight

$$\eta_r = (1 + aC)^k \quad (ii)^8$$

$$\eta_r = (1 + a'C)^6 \quad (iii)^9$$

Equation (iii) has been used to represent the experimental data in Table I, and the fluidities recorded in it under the column headed "calculated" are derived from this equation with values of  $a'$  equal to 0.091 for the untendered silk, and 0.0467 for the tendered. There is seen to be reasonable agreement between the experimental and calculated fluidities.

Table I

UNTENDERED SILK			TENDERED SILK		
$C$ (gm per 100 cm)	Fluidity		$C$ (gm per 100 cm)	Fluidity	
	Calculated	Found		Calculated	Found
6.0	5.44	{ 5.11	6.0	16.9	16.6
		{ 5.08	5.55	18.6	18.8
5.55	6.39	{ 6.54	5.0	21.1	21.1
5.0	7.82	{ 7.87	4.42	24.1	24.1
4.42	9.78	{ 7.70	4.0	26.5	26.5
		{ 9.70			
4.0	11.53	{ 11.62			
		{ 11.32			
3.0	17.4	{ 17.95			
2.0	27.2	{ 28.2			
1.0	43.8	{ 43.8			

The most significant constant in Baker's equation is the product  $ak$  or  $6a$  in equation (iii). This is the limit, as  $C$  approaches zero, of  $(\eta_r - 1)/C$  (or  $\eta_{sp}/C$ ) and is the viscosity function related by Staudinger to the molecular weight of the dissolved polymer. For the untendered and tendered silks, the limiting values of  $\eta_{sp}/C$  are thus 0.546 and 0.28, respectively, concentrations being expressed in grams per 100 c.c.

When the silk is not available in quantity sufficient for the preparation of a 5 per cent. solution, its fluidity can be measured at a lower concentration and the result calculated to the standard 5 per cent. by means of equation (iii).

Finally, it is of interest to note that neutralised solutions of silk of fluidity 5, 14, and 40 give values of  $t_1/t_2$  which are very near unity, when examined in the B.C.I.R.A. cellulose viscometer. Thus, 5 per cent. silk solutions show much smaller deviations from Poiseuille's law than do 0.5 per cent. cellulose solutions.

The fluidity determinations recorded in this paper were carried out by Mr. P. Cole.

## REFERENCES

- <sup>1</sup> Clibbens and Geake *Shirley Inst Mem*, 1927, 6, 117-132, or *J Text Inst*, 1928, 19, T77-92
- <sup>2</sup> Clibbens and Little *Shirley Inst Mem*, 1936, 15, 25-44, or *J. Text. Inst*, 1936, 27, T285-304
- <sup>3</sup> Trotman and Bell *J Soc Chem Ind*, 1935, 54, 141-142T
- <sup>4</sup> Trotman *J Soc Chem Ind*, 1936, 55, 325-327T
- <sup>5</sup> Tweedie. *Canadian J Res*, 1938, 16B, 134-150
- <sup>6</sup> Takamatsu *et al* *J Soc Chem Ind Japan*, 1932, 35B, 14-16, 1933, 36B, 566-568, 596-604, 662-668, 668-672
- <sup>7</sup> Baker *J Chem Soc*, 1913, 103, 1653-1675
- <sup>8</sup> Philippoff and Hess *Z physikal Chem*, 1936, B31, 237-255
- <sup>9</sup> Bredee and De Booy *Kolloid Z*, 1937, 79, 31-43

Received 26/10/40

## 2—THE FLUIDITY OF SILK SOLUTIONS

### Part II. APPLICATION

By CHARLES JOHN CADWALLADER, M A , B Sc ,  
FREDERICK OLIVER HOWITT, Ph D., F I C , F.T I., and  
STUART GRAYSTON SMITH, Ph D

(The British Cotton Industry Research Association Silk Section)

(Copyright by The Textile Institute)

#### I. Introduction.

In the preceding paper, the determination of the fluidity of silk in cupri-ethylenediamine solution was described and it was stated that a fluidity range of approximately 4 to 50 is obtained for untendered silk and silk tendered until the tensile strength approaches zero. The purpose of the present paper is to describe the relationships existing between fluidity and tensile strength of silks tendered to varying extents and by different chemical reagents and to indicate the value of fluidity determinations in appraising the approximate retention of strength by silk yarns or fabrics which have experienced chemical treatment parallel to that operating in commercial practice. In addition to the economy in time and material that the fluidity method has over the direct examination of tensile strength, the determination of fluidity considerably amplifies the somewhat limited information given by determinations of breaking load. Thus if a silk warp yarn, taken from a woven silk fabric, has a low fluidity and a low breaking strength, the conclusion can be drawn that it is very probable that the yarn has experienced mechanical damage in the loom, such a conclusion would be supported by the weft threads having low fluidity and high tensile strength.

In the production of dyed silk fabrics, either woven or knitted, many processes are used in which the possibility of chemical degradation of the fibre is present. This is especially true of the discharging and dyeing processes. In some works, it is a common practice to add soda ash to the soap liquor used for degumming and, unless this addition is carefully controlled, a small but significant loss of strength of the material occurs. Such a loss of strength is perhaps by itself not serious but an accumulation of four or five of these losses results in the final material having a strength as low as one-half of that which would result from careful treatment at every stage of its manufacture.

This retention of the greater part of the initial strength of silk merits close attention. During the present decade, the strength of artificial fibres has been improved to such an extent that the tensile strength of silk has been equalled and it is evident that, if silk is to maintain its unique position amongst the textile fibres by virtue of its strength, lustre, handle, etc., its advantages in one or more directions must not be allowed to be offset by a serious failing in its tensile strength.

The loss in strength of silk due to chemical degradation of fibroin occurs in a more insidious manner than does that due to mechanical degradation. All silk manufacturers appreciate the danger of using sand or emery rollers on the loom but few appear to give sufficient consideration to the effects of prolonged exposure to alkaline discharging baths or finishing baths of excessive acidity. Up to the present, this has been largely due to the lack of a test for chemical damage which can be readily applied and is of adequate sensitivity. The fluidity test for silk described in the preceding paper will it is hoped, at least partly fulfil this requirement.

At present, the fluidity test is applicable to degummed silk (of the *Bombyx* type, tussah silk is only partly soluble in the solvent) and to silk which has been degummed and dyed, with or without a small amount of tannin or mineral mordant. The test cannot be applied directly to tin-weighted silk owing to the formation of a gelatinous precipitate on dissolution in the cupri-ethylenediamine reagent. The possibility of removing the weighting material from tin-weighted silk without affecting the fluidity of the fibroin is being investigated. All values of fluidity are given in reciprocal poises at 20° C. For each sample, the single value given is the mean of two or more values which are in close agreement.

## II. Raw Filature and Waste Silks

Each sample examined was degummed in a 1 per cent solution of soap flakes (liquor to silk ratio approximately 200) for one hour at a gentle boil, steeped in distilled water at 95-100° C, washed in several changes of warm distilled water, and finally dried at 30° C and conditioned at 65° F and 65 per cent relative humidity. The results are given in Table I. The stored samples of raw filature silk (Nos. 1-11) gave fluidities of 5.9 to 8.7, the lowest value of 5.9 being given by a sample which had been stored for 10 years without any special protection apart from that afforded by its package in a paper envelope and cardboard box. Recently produced silks (Nos. 12-20) gave fluidities of 6.0-8.0. In connection with the fluidity of degummed filature raw silk, it is of interest to record that the lowest fluidity so far obtained is 3.8, a value given by a carefully degummed, 90 per cent. Jap filature, with this sample, the period of dissolution was reduced from three minutes to one minute. Three unclassified silks (Nos. 21-23), which by their appearance and normal solubility in cupri-ethylenediamine reagent are considered to be semi-wild silks of the *Bombyx* type, gave higher fluidities of 11.0-13.5.

The data for silk wastes, compared with those for filature silks, are of interest. Six samples of wastes (Nos. 24-29) of recent production and of types commonly used by silk spinners in this country, gave fluidities 4.6-8.0. A tinted (throwsters') gum waste (No. 30) gave a value also within this range but two other samples (Nos. 31 and 32), which had been stored for 1-2 years and one of which was extremely oily, gave much higher values of 15.4 and 15.9. Spinners' drafts (Nos. 33 and 34) prepared from a throwsters' waste of a greasy character gave fluidities of 13.2 and 14.8.

## III. Silk Yarns

Nett silk yarns, after the soaking and throwing processes, are often stored for several months before being used in weaving, with yarns for knitting, storage is minimised as far as possible. The data included in Table II are indicative of the changes occurring in soaked silk on prolonged storage. Samples 1-8 were prepared from the one bale of raw silk (13/15-den. Japan) and all have been stored on bobbins kept in cardboard boxes at room temperature for three years. After this time, the unsoaked raw silk (No. 7) gave a fluidity of 6.8, whilst the soaked raw gave a fluidity of 10.5. Degumming of the corresponding soaked 2-, 4-, and 6-thread yarns (Nos. 1-3) of low twist by boiling in 1 per cent soap solution for one hour, gave yarns of fluidity 11.3 to 13.7, whilst the yarns of higher twist (Nos. 4-6), after degumming for six hours in boiling 1 per cent. solution (for such high twists, the minimum conditions for complete discharge) gave fluidities of 18.9 to 22.1. This laboratory degumming was carried out with ratios of liquor to

silk of not more than 200 to 1. It is apparent that (a) the storage of thrown yarns in the soaked condition may result in chemical tendering and (b) the complete degumming of high twist yarns is accompanied by a certain degree of tendering. This latter tendering is probably due to the external surface of the yarn being degummed at an early stage of the process and hence exposed to the tendering action of the degumming medium, such an exposure is unavoidable owing to the prolonged degumming necessary to remove the gum from the interstices of the tightly packed filaments.

Table I

Sample number	Type	Date received	Fluidity
(a) STORED RAW FILATURE SILKS.			
1	Yellow Japan	1929	5.9
2	Canton Filature	1933	8.5
3	Italian	1933	8.7
4	20/22 Italian Exquis	1934	6.6
5	Hard-natured Japan	1936	7.5
6	Soft-natured Japan	1936	8.0
7	18/20 China	1936	8.3
8	Italian	1936	8.5
9	Italian Grand Exquis	1937	7.7
10	China	1937	6.1
11	23/25 Italian Grand Exquis	1938	6.8
(b) RAW FILATURE SILKS OF RECENT PRODUCTION (1937-1938)			
12	10-den White Italian	1939	6.7
13	14-den Yellow Italian	1939	8.0
14	14-den White Hungarian	1939	6.9
15	14-den Russian	1939	6.4
16	17-den. Japan	1939	6.0
17	21-den White Caucasian	1939	6.1
18	22-den Kashmir	1939	7.0
19	22-den Canton	1939	6.1
20	24-den China	1939	7.2
(c) WILD AND UNCLASSIFIED SILKS OF <i>Bombyx</i> TYPE			
21	African (?) origin	1938	11.0
22	Sudan	1929	11.4
23	Peru	1928	13.5
(d) SILK WASTES			
24	China Steam Waste	1939	4.6
25	White Knubbs	1939	5.0
26	American Gum Waste	1939	6.0
27	Jap Gum Waste	1939	6.6
28	China Gum Waste	1939	8.0
29	Yellow Knubbs	1939	6.4
30	Tinted Gum Waste	1939	5.1
31	Throwsters' Waste (Greasy)	1938	15.9
32	Throwsters' Waste	1938	15.4
33	Drafts from Throwsters' Waste	1938	13.2
34	Drafts from Throwsters' Waste	1938	14.8

A soaked organzine yarn (No. 9) of more recent production gave fluidity 10.5

A series of commercially dyed, nett silk yarns (Nos. 10-17) which had been stored for varying periods, gave fluidity values of 14.8-33.0. The results show that the relative degradation of the yarns on storage is independent of the duration of storage and that the method of finishing is probably the main factor, owing to lack of knowledge regarding the final processing treatment, no correlation with the fluidities of the samples is possible. With



Table II

Sample number	Description and treatment	Date received	Fluidity
STORED SOAKED THROWN YARN			
1	2-thread, 10 t p 1	1936	13.7
2	4-thread, 10 t p 1	1936	13.5
3	6-thread, 10 t p 1	1936	11.3
4	2-thread, 90 t p 1	1936	22.1
5	4-thread, 80 t p 1	1936	20.2
6	6-thread, 70 t p 1	1936	18.9
7	Unsoaked, raw 13/15-den.	1936	6.8
8	Soaked, raw 13/15-den	1936	10.5
9	Soaked 22/24 China organzine in gum	1938	10.5
COMMERCIALY DYED NETT YARNS *			
10	Sulphuric acid-thiourea treatment	1929	14.8
11	Sulphuric acid treatment	1930	16.4
12	Formic acid treatment	1930	17.5
13	No after-treatment	1913	18.3
14	No after-treatment	1930	23.7
15	Sulphuric acid treatment	1923	29.3
16	Formic acid treatment	1923	30.0
17	No after-treatment	1935	33.0
UNDYED SPUN YARNS			
18	First quality 16/3	1939	14.2
19	14/3 spun yarn	1936	17.3
20	First quality 60/2-Schappe	1931	17.9
21	French Schappe 60/2	1936	18.8
22	Second quality 60/2	1931	19.2
23	Standard quality 60/2	1931	20.8
24	Second quality Schappe 60/2	1931	23.8
25	Italian Schappe	1936	25.5
26	Spun yarn—A	1939	15.1
27	Spun yarn—B	1939	14.4
28	Spun yarn—C	1939	13.2

\*For samples 10-17, the date given refers to date of production

undyed spun yarns, the fluidity should be identical with that of the degummed waste apart from the possible increase in fluidity due to gassing and scouring (including bleaching) treatments. The samples examined (Nos. 18-28) gave fluidities ranging from 13.2 to 25.5. These values appear to be unduly high, bearing in mind that a good quality degummed waste (e.g., knubbs or steam waste) has fluidity approximately 6-8. It is unlikely that a normal gassing and soap-scouring treatment is sufficient to account for the large increase in fluidity and the commercial degumming and bleaching (if any) must therefore be regarded as the cause of the greater part of the chemical tendering. The effect of exposure to a degumming medium is an important consideration in the degumming of Macclesfield crêpe cloth in which the discharge of the gum applies to only the crêpe weft, the spun warp yarns are in the degummed condition and hence are exposed to boiling soap solution during the whole period of discharge treatment. That such an exposure produces a significant tendering of the warp yarns is shown by the data in Table III, in which are given the fluidity and retained strength of a 60/2 spun silk yarn immersed in boiling 1 per cent soap solution for varying periods of time. It will be noted that, with the yarn examined, an increase in fluidity from 13.5 to 20.7 is accompanied by a loss in strength of approximately 17 per cent. Similar changes in fluidity and tensile strength have been demonstrated for the warp yarn *in situ* in a Macclesfield crêpe yarn.

The schapping process appears to have a tendency to give yarns of comparatively high fluidity (Nos. 21, 24, and 25, in Table II).

Table III

Sample number	Time of boiling (hours)	Percentage retained strength	Fluidity
1 (control)	0	100	13.5
2	1	98.7	14.1
3	2	92.2	14.7
4	3	90.6	16.4
5	4	88.0	17.1
6	6	84.8	18.7
7	8	83.4	20.7

## IV. Parachute Fabrics

Parachute fabrics are of special interest from a fluidity view-point owing to the possibility of the fluidity test affording a criterion of the suitability of the finished material to withstand the exacting stresses imposed on it during use. The silk cloth employed for parachutes receives a simple degumming and washing treatment and hence dissolves in the cupri-ethylenediamine reagent without leaving any residue and gives accurate and reproducible fluidity values.

In Table IV are given the fluidities of parachute fabric of recent production (Nos 1-8) and those of fabrics (Nos 9-15) which have been stored away from the light for a period of approximately three years.

Table IV

1938-1939 Production		Samples stored for 3 years		Damaged material	Fluidity	
Sample Number	Fluidity	Sample Number	Fluidity	Sample Number	Undamaged portion	Damaged portion
1	5.5	9	9.6	16	19.0	39.2
2	7.0	10	12.1	17	27.3	38.4
3	7.6	11	13.8	18	34.7	39.3
4	8.0	12	14.2	19	12.6	18.5
5	8.8	13	15.2	20	16.4	28.0
6	9.6	14	17.9	21	17.6	26.9
7	10.1	15	20.4	22	23.5	33.7
8	12.6					

The fluidities of the cloths in the first groups are mainly below 10, and, in view of the fluidity 5-8 given by good quality raw silks which have been carefully degummed and washed, the fluidity for parachute cloth will not greatly exceed these figures. The fluidities of the stored samples show that assuming the initial fluidities were generally less than 10, the samples have, with one exception, deteriorated to slight and varying extents. The sample showing a fluidity of 20.4 (No 15) was initially below specification strength and the stored sample was re-examined for tensile strength. After dissection of the cloth, the warp yarn gave fluidity 21.9 and breaking load 0.62 gm per denier whilst the weft gave fluidity 20.9 and breaking load 2.68 gm per denier. A good quality silk yarn, which is undamaged chemically or mechanically, has a strength of 4.5 gm per denier and, as indicated above, a fluidity of 5-8. It therefore follows that both warp and weft are chemically tendered and that the warp is seriously mechanically damaged, this mechanical damage probably occurred during weaving.

The third part of Table IV gives fluidity data for parachute fabrics in which damage has been caused during use (Nos 16-18) or has been simulated in the laboratory (Nos 20-22). The first group had received

some form of chemical contamination associated with the development of localised brown stains, the tendering of the fabric shown by the fluidity values was found to be reflected in the decrease in the bursting strength. The laboratory stains and accompanying tendering were produced by wetting a normal parachute cloth with sea-water and then heating the samples in small stainless-steel autoclaves for 48 hours at 90° C. This procedure appears to be of promise in the testing of silk material for the presence of injurious chemical substances and is being further investigated.

Sample 19 is a silk sewing thread used in a partly stained seam of a defective parachute and here again the staining is associated with chemical tendering of the silk as evidenced by the change in fluidity.

#### V. Commercial Silk Fabrics

Tables V and VI give fluidity values for two series of commercial silk fabrics

The first series consist of cloths which have been stored, without special precautions, for periods varying from a few months to about 5 years. With these samples, breaking load determinations have been carried out on the warp and, where possible, on the weft yarns. The fluidities of two samples (Nos 1 and 8) are satisfactory but the period of storage of these two samples has been comparatively short, with sample 8, the strengths of 1.96 and 3.26 gm. per denier for warp and weft yarn, respectively, indicate that the warp has been mechanically damaged, no doubt during weaving. Three samples (Nos 3, 4 and 5) show a considerable degree of tendering, both in warp and weft, the breaking load figures for the three warps indicate that no appreciable mechanical damage has occurred. The conclusion that mechanical damage has taken place during weaving is applicable to sample 6.

Table V

Sample number	Type of cloth	Date of weaving	Warp		Weft	
			Tensile strength (g per denier)	Fluidity	Tensile strength (g per denier)	Fluidity
1	Crêpe (undyed)	1938	2.08	11.9	—	12.4
2	Fancy crêpe (undyed)	1935	3.44	18.3	—	18.3
3	Crêpon (pastel pink)	1934	2.08	27.1	2.33	26.6
4	Crêpe satin (ivory)	1934	2.06	29.3	—	28.9
5	Crêpon satin (deep green)	1934	2.77	29.3	—	26.9
6	Fancy cloth (blue)	1934	1.91	20.9	3.30	19.7
7	Plain cloth (pastel pink)	1936	1.69	18.0	—	17.7
8	Crêpe (undyed)	1939	1.96	13.6	3.26	13.2

in which, for equal fluidities, the warp and weft yarns show strengths of 1.91 and 3.30 gm per denier, respectively. Mechanical damage has also occurred in the warp of sample 1 (fluidity 11.9, strength 2.08 gm per denier) and, perhaps, to a smaller extent in that of No. 7 (fluidity 18.0, strength 1.69 gm. per denier).

The second series of cloths were samples of recent production (probably 1938-1939). Table VI records the fluidities of these cloths and, to indicate the approximate cloth density, the number of picks and ends per inch. Of the 24 samples examined, only one (No 18) gives a fluidity below 10, the remainder may be grouped as follows:—

5	with a fluidity between 10 and 15.
12	“ “ “ “ 15 and 20
5	“ “ “ “ 20 and 25.
1	“ “ “ “ 25 and 30.

Table VI

Sample number	Type of cloth	Picks per inch	Ends per inch	Fluidity
1	Jappe (dyed)	108	116	12.5
2	Plain crêpe (dyed)	110	148	12.2
3	" " "	140	140	15.9
4	" " "	120	170	19.8
5	" " "	136	148	19.3
6	" " "	106	120	29.4
7	Printed crêpe	84	164	16.1
8	" "	112	152	22.7
9	" "	106	164	23.6
10	" "	90	148	22.0
11	" "	120	154	21.3
12	" "	108	154	17.7
13	" "	94	154	17.2
14	" "	120	162	15.4
15	" "	94	156	20.2
16	Georgette (printed)	118	120	11.2
17	" (dyed)	120	130	16.5
18	" "	102	124	9.1
19	Crêpon (printed)	126	176	15.4
20	Crêpe satin (dyed)	118	378	16.9
21	" " "	112	456	12.4
22	" " "	130	448	16.9
23	" " (printed)	116	370	18.3
24	Brocade (dyed)	102	180	13.1

The fluidity of sample 6, namely 29.4, must be considered as unsatisfactory and, bearing in mind the fluidity range obtainable with normal, undyed yarns, it would appear that the processes resulting in a fluidity of 20-30 in these cloths should be critically examined, although it is recognised that the service demanded of the fabric is a deciding factor in its commercially acceptable strength and wearing properties.

#### VI. Silk Hosiery Fabric

Table VII gives the fluidities of various samples of silk hosiery of different grades. The first series (Nos 1-6) is of unused, dyed stockings which have been stored for periods up to approximately two years. For this series, all the values fall between 8 and 10.5. The second series (Nos 7-12) is of pairs of stockings recently purchased at retail shops and which include both circularly knit and full-fashioned samples. For these stockings fluidities are given for the samples as received and after 10 and 20 washes, respectively, each washing treatment consisted of gentle agitation in 1 per cent solution of soap flakes at 40-50° C for about 5 minutes, followed by washing in tap water (hardness 3-4 degrees) and drying at room temperature. The fluidity of each stocking (designated as R and L, respectively) of the pair is given. The results show a greater variation than that occurring in the first series. The lowest value, 4.4, for sample 9R is surprisingly low for a dyed and finished silk material whilst the highest value, 17.2, for sample 8L must be regarded as unsatisfactory. The quality of the stocking, as evidenced by price and method of knitting, was not related to the quality of the silk as indicated by fluidity. An interesting feature is the slight but general decrease in fluidity after 10 washes, this decrease is possibly due to removal of substances incidentally or purposely left on the threads after the finishing treatment. A further 10 washes gives fluidities approximating to the initial

Table VII

TABLE VII

Sample number	Description	Fluidity		
MISCELLANEOUS DYED, UNUSED SAMPLES				
1	Received 1938	8 0		
2	" 1937	9 0		
3	" 1939	10 1		
4	" 1939	10 1		
5	" 1938	10 5		
6	" 1937	8 3		
1939 PRODUCTION, DYED, UNUSED SAMPLES				
		As received	After 10 washes	After 20 washes
7	Brand A { <sup>L</sup> <sub>R</sub>	10 2 9 8	9 9 9 7	10 5 9 8
8	Brand B { <sup>L</sup> <sub>R</sub>	17 2 16 0	16 9 14 6	16 6 16 2
9	Brand C { <sup>L</sup> <sub>R</sub>	6 3 4 4	6 2 5 0	6 1 5 2
10	Brand D { <sup>L</sup> <sub>R</sub>	12 4 12 3	11 3 11 3	12 6 13 6
11	Brand E { <sup>L</sup> <sub>R</sub>	10 8 10 9	9 8 10 2	10 8 11 2
12	Brand F { <sup>L</sup> <sub>R</sub>	8 2 8 4	6 8 6 7	7 1 7 0
SAMPLES WHICH HAVE RECEIVED FREQUENT WEAR AND MANY WASHES				
		Top	Knee	Ankle
13	—	12 3	12 8	12 9
14	—	12 8	12 8	13 7
15	—	13 3	13 8	15 2
16	—	11 5	11 9	14 0
17	—	12 1	12 9	12 7
18	—	11 3	11 4	12 1

values. It follows that the intrinsic strength of the silk filaments is not diminished in any way by appropriate washing treatment. This conclusion is confirmed by the results of the third series (Nos. 13-18) which consists of stockings finally discarded after eighteen months of normal service during which period they had been washed some 150-200 times. The fabric from ankle, knee, and top parts of the silk panel gave fluidities within the range of 11.3 to 15.2, indicating that only slight chemical tendering had occurred. The data give a descending order of fluidity of ankle, knee, and top parts of the fabric, this difference, admittedly small, is probably due to the difference in exposure of the different parts of the fabric to atmospheric conditions, splashes from the road, etc.

#### VII. Acid- and Alkaline-treated Silk Yarns

In the preceding part of this paper, consideration has been given to the fluidity values yielded by commercial samples of raw silk, yarns and fabrics without direct qualification as to their tensile strength. During the degumming, dyeing, and finishing treatment of silk, the reagents used may, as regards their possible tendering action on silk, be classified in most instances as acids or alkalis. In order to determine the relationship between tensile strength and fluidity of silk which had been treated to varying extents with acid or alkali, "cut-skein" hanks of degummed, 4-13/15 yarn of 6 turns

per inch were immersed in 0.1*N*-acid or -alkali for varying periods of time, washed, and dried. As acids, sulphuric and hydrochloric acids and, as alkali, sodium hydroxide were used. The alkali solution was found to tender at a greater rate than did the acid solutions and hence the former was used at 80° C and the latter were used at 90° C in order to give comparative times of treatment. The three series of experiments (i.e., hydrochloric acid, sulphuric acid, sodium hydroxide) were repeated twice and each hank of 50-100 threads was examined for breaking load and fluidity; one

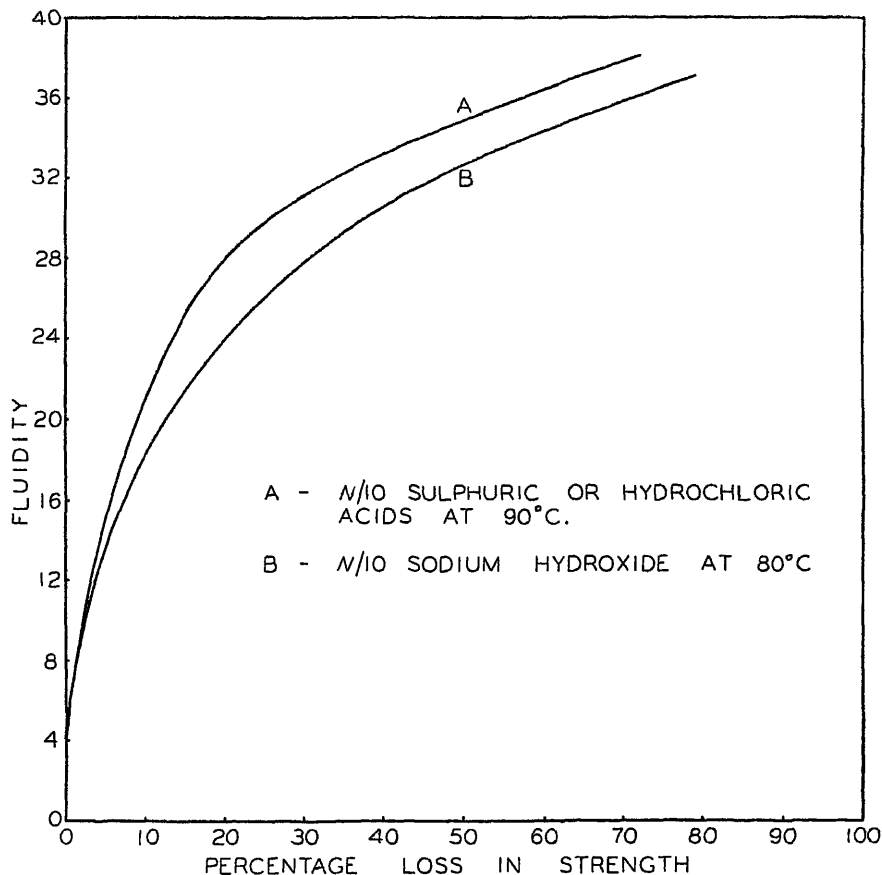


Fig 1  
Relation between fluidity of silk and percentage loss in strength due to treatment with dilute acid or alkali

hank of each series was not treated and served as a control for the tensile strength of the yarn. The data thus obtained are given in graph form in Fig 1. The results from the treatment by the two acids were, within the limit of experimental error, identical. The curve A represents the general trend of a close scatter of points from all the acid series, whilst B represents the corresponding trend for the alkali series.

It will be seen from these curves that the relationship between tensile strength and fluidity for alkali-tendered silk is not identical with that for acid-tendered silk. This is in agreement with the conclusions of Tweedie,<sup>1</sup> Jordan Lloyd<sup>2</sup>, and others that the hydrolysis of silk by dilute acid follows a

route different from that by dilute alkali. The difference, however, is not sufficiently great to prohibit the deduction of an approximate value of the strength of a silk yarn from its fluidity, providing that the yarn is known to be tendered by either acid or alkali acting in aqueous media. The initial increase in fluidity with loss in strength is relatively great, thus a loss of 5 per cent of the original strength of the yarn increases the fluidity from 4 to about 12. The fluidity may increase to the region of 20 before the loss of strength becomes serious and above this value any increase in fluidity is attended by a significant drop in tensile strength.

Approximately one half of the tensile strength of the yarn is lost when the fluidity reaches a value of 30-35.

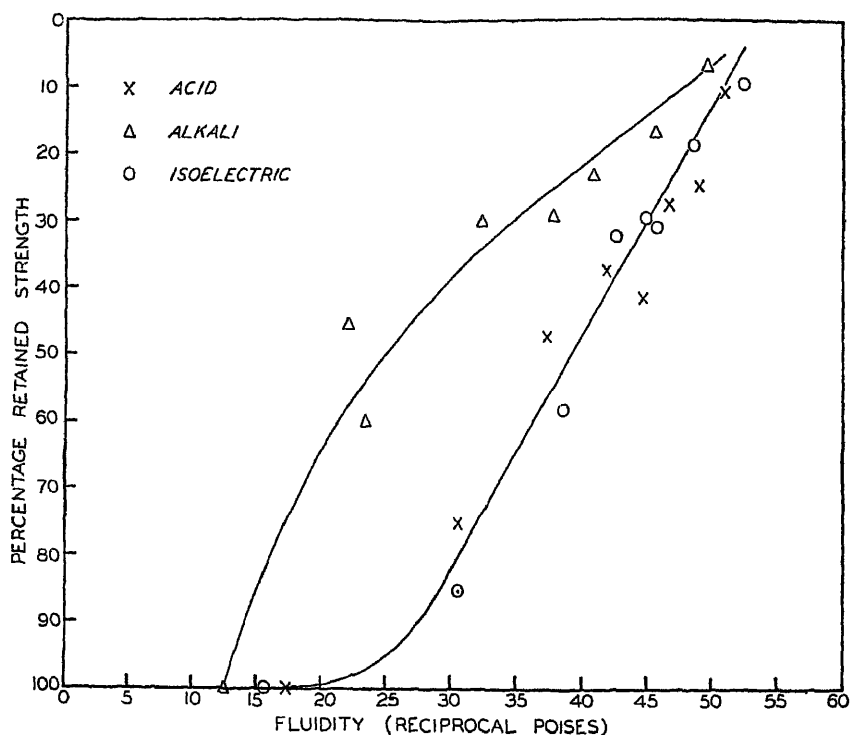


Fig. 2

Tensile strength/fluidity relationship for silk tapes finished at acid, alkaline and isoelectric reactions and subsequently heated to 130° C for different times

#### VIII. Heat-tendered Silk Tape

Silk, in common with other fibres, is slowly tendered on exposure to temperatures above, but not far removed from, that of boiling water. The maximum temperature to which silk is exposed during any commercial process is, so far as can be judged, within the range of 120-140° C. In addition to the effect of temperature alone, the condition of the silk as regards presence of acid, alkali, mineral salts, etc., must be considered as an important factor in heat tendering. The following experiment covers, to some extent, the effect of exposure of silk finished in different ways to a relatively high temperature (viz, 130° C.). The silk used was in the form of a quarter-inch tape, carefully degummed in soap solution, well washed, and

then brought to an isoelectric condition by soaking in a large excess of dilute ( $N/150$ ) acetic acid and washing in many changes of warm, distilled water until free from acid, it is necessary to continue this washing treatment for several days in order to remove all traces of acid. The material thus obtained had an ash content of approximately 0.05 per cent. A skein of the tape was then prepared and cut so that three hanks, each containing eight comparable samples, were obtained. Each sample contained ten lengths of  $10\frac{1}{2}$  inches each, for comparative breaking-load determinations. One hank was soaked in 2 litres of 0.02*N*-sulphuric acid for 24 hours, another in the same volume of 0.02*N*-sodium hydroxide, and the third retained in the isoelectric condition. Two small auxiliary hanks which had been included in

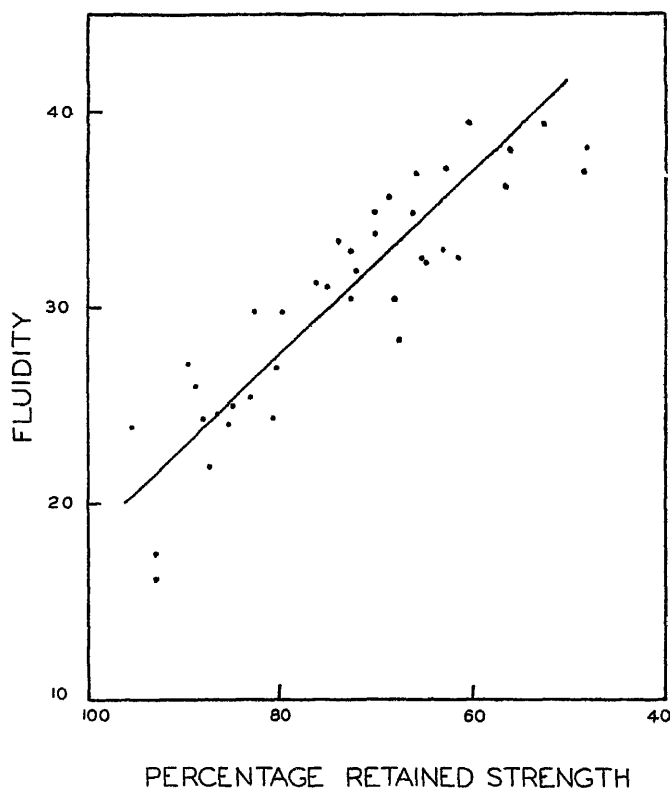


Fig. 3

Curve showing relationship between strength and fluidity for light-tendered silk

the soaking treatment with acid or alkali were used to afford a comparative idea of the amount of acid and alkali combined by measurement of the  $pH$  of their aqueous extracts (20 : 1 liquor : silk ratio). The  $pH$  values of these extracts as measured on the glass electrode were, for the acid-treated silk, 2.76, and for the alkali-treated silk, 11.50.

After attaining equilibrium with the acid or alkali, one sample of each of the three hanks (acid, alkaline, and isoelectric) was retained as a control for breaking load determinations, whilst the remaining samples were heated in an oven at a controlled temperature of  $130^{\circ}C$  for periods varying from 7 to 312 hours. After heating for an appropriate time, the samples were removed and their tensile strength and fluidity determined. It was found



that, whilst all the acid-treated and isoelectric samples dissolved normally in the cupri-ethylenediamine reagent, the alkali-treated samples which had been heated for 7, 24, and 48 hours did not dissolve readily, 5-10 minutes in place of the usual 3 minutes being necessary in order to effect dissolution. This anomaly is reflected in the curves showing the relationship between retained strength and fluidity (Fig 2). Thus, whilst the acid-treated and isoelectric samples approximately fall on the same curve, the fluidities of the alkali-treated samples at first widely diverge from, and then tend towards coincidence with, this curve. It is of interest to compare these curves with those given by treatment with wet acid and alkali (Fig 1). The effect of acid or isoelectric reactions at 130° C approximately coincides with that of wet acid from the initial state until the point at which only about 40 per cent of the initial tensile strength is retained, after this, there is an upward trend of the curve, low retained strength being accompanied by relatively higher fluidities. With regard to the alkali-treated samples, similarity between the behaviour of dry-heated and wet-heated samples is vitiated by a secondary effect due to heating the dry sample in the presence of alkali. This effect implies a considerable modification in the properties of the silk for not only is the solubility in cupri-ethylenediamine reagent diminished, but the fluidity, at the stage when the effect is maximal, tends to decrease with decrease in tensile strength. The anomaly disappears as the silk is further degraded by the heat treatment and it is possible that the chemically modified form of the silk is broken down by a mechanism quite distinct from that involved in its formation. The most likely cause of the phenomenon is that of formation of a degradation product of fibroin equivalent to a metaprotein and this aspect is being further investigated.

The occurrence of abnormally low fluidities due to alkali treatment and subsequent exposure to high temperatures is very unlikely in commercial practice. It follows, therefore, that the same approximate relationship between fluidity and tensile strength may be assumed to hold generally for commercial samples which have received some form of acid or alkali treatment during finishing.

#### IX. Light-tendered Silk Yarn

The susceptibility of silk to degradation by light is often a factor in the utility of silk fabrics and the assessment of photochemical tendering by the fluidity method is therefore of importance. In a series of experiments that were carried out in order to elucidate the mechanism of the degradation of silk by light, data showing the relationship between the strength and fluidity of a silk yarn (degummed 4-thread 13/15-denier Japan) were obtained. These data, which cover different periods of exposure and varying degrees of acidity and alkalinity in the yarn, are represented in Fig 3 and show that the correlation existing between the values of retained tensile strength and the corresponding fluidities justifies the application of the fluidity test as a criterion of the chemical integrity of silk that has been exposed to light.

---

The fluidity measurements recorded in this paper were carried out, in part, by Miss M. Wright.

#### REFERENCES

- <sup>1</sup> Tweedie *Canadian J. Res.*, 1938, 16B, 134-150.
- <sup>2</sup> Jordan Lloyd *Trans. Faraday Soc.*, 1935, 31, 317-324.

# THE JOURNAL OF THE TEXTILE INSTITUTE

## TRANSACTIONS

### 3—THE DISSOLUTION OF CHEMICALLY MODIFIED COTTON CELLULOSE IN ALKALINE SOLUTIONS. PART VI. THE EFFECT OF THE METHOD OF MODIFICATION ON THE RELATION BETWEEN FRACTIONAL SOLUBILITY IN SODIUM HYDROXIDE SOLUTION AND FLUIDITY IN CUPRAMMONIUM SOLUTION.

By T. BROWNESETT and G. F. DAVIDSON  
(The British Cotton Industry Research Association)  
(Copyright by The Textile Institute)

#### INTRODUCTION

In a previous paper<sup>1</sup> dealing with the dissolution of chemically modified cotton cellulose in cold sodium hydroxide solutions it was shown that the relation between fractional solubility (defined as the percentage of the material dissolved under standardized conditions) and fluidity in cuprammonium solution was not the same for all types of modified cotton, but depended on the method of modification and on whether the cotton had been mercerized before modification. The present paper describes a more comprehensive investigation of the effect of the method of modification on the solubility-fluidity relation, the materials studied comprising nine different types of modified cotton. The solubility measurement employed was the determination of the percentage of the modified cotton dissolved by 2.5*N* sodium hydroxide solution at  $-5^{\circ}\text{C}$ . Under these conditions an unmodified cotton is almost completely insoluble and the most highly modified materials considered show a solubility approaching 100 per cent., so that the whole of the solubility scale is utilized.

#### DESCRIPTION AND DISCUSSION OF RESULTS

The modified cottons employed consisted of a series of hydrocelluloses and eight series of oxycelluloses prepared by the action of (1) alkaline hypobromite, (2) alkaline hypochlorite, (3) neutral hypochlorite, (4) acid hypochlorite, (5) dichromate in the presence of sulphuric acid, (6) dichromate in the presence of oxalic acid, (7) periodic acid, and (8) metaperiodate.

The relations between alkali-solubility and fluidity for the various types of modified cotton are shown graphically in Figs. 1A and 1B. In a comparison of the various relations it is convenient to employ that given by the hydrocelluloses as a standard, and for this purpose the hydrocellulose curve is included in both Figs. 1A and 1B. It is seen that no two types of modified cotton give exactly the same relation between fluidity and solubility, but the curves for the alkaline hypobromite, the alkaline hypochlorite and the two dichromate series of oxycelluloses do not differ greatly from that for hydrocelluloses. The neutral hypochlorite oxycelluloses are, for a given fluidity, considerably more soluble than these five types, and this abnormally high solubility is shown in an even greater degree by the acid hypochlorite

series; this behaviour is in qualitative agreement with that previously found for oxycelluloses prepared by the action of hypochlorite at pH 8.4<sup>1</sup> Periodic acid and metaperiodate oxycelluloses, on the other hand, are con-

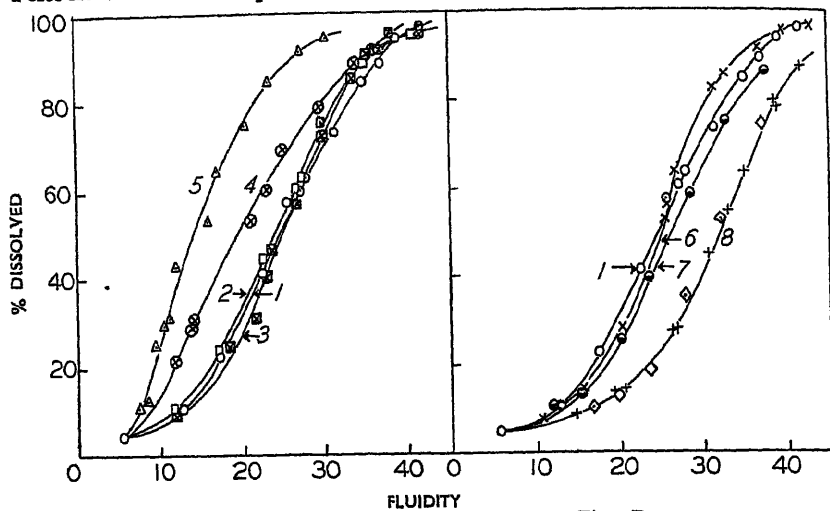


Fig. 1A

Fig. 1B

Fluidity-solubility relations for cottons modified by the action of (1) hydrochloric acid, (2) alkaline hypobromite, (3) alkaline hypochlorite, (4) neutral hypochlorite, (5) acid hypochlorite, (6) dichromate and sulphuric acid, (7) dichromate and oxalic acid, and (8) periodic acid or metaperiodate.

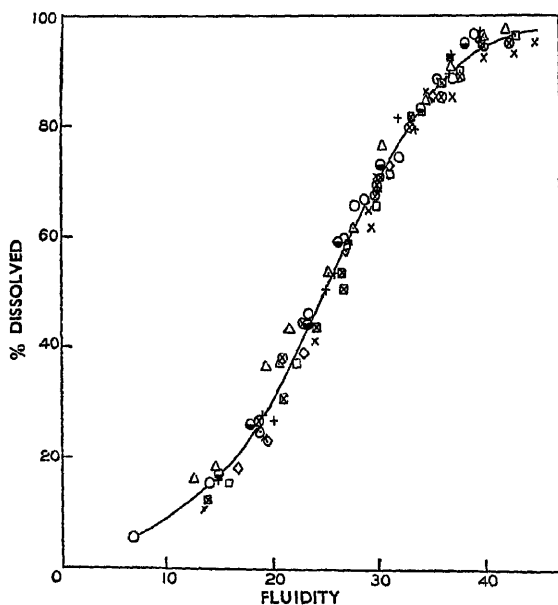


Fig. 2. Fluidity-solubility relations for modified cottons of nine different types after boiling under pressure with sodium hydroxide solution.

siderably less soluble than hydrocelluloses of equal fluidity. A single curve suffices to describe the fluidity-solubility relation for both these types of oxycellulose, and since they also behave similarly in other respects<sup>2</sup> it will be convenient to group them together as "periodate" oxycelluloses

When the modified cottons are boiled under pressure with 0.25*N* sodium hydroxide solution the differences illustrated in Figs. 1A and 1B largely disappear, and the relation between the fluidity and the solubility of the boiled materials of all types may be expressed by a single curve (Fig. 2) which is almost coincident with the curve for unboiled hydrocelluloses. A similar result is also achieved by pre-treatment of the modified cottons with 0.1*N* sodium hydroxide solution for 24 hours at 20°C.

The effects of the hot and the cold alkaline treatments on the fluidity and the solubility of a given type of modified cotton are in general similar, but these effects vary greatly with the method of modification (Table I).

Table I

Method of modification	FLUIDITY			% DISSOLVED			
	Original modified cotton	After pre-treatment A	After pre-treatment B	Original modified cotton	After pre-treatment A	After pre-treatment B	After pre-treatment C
Periodic acid	20.4	20.0	19.1	14.1	26.8	25.0	23.4
	26.5	25.7	24.8	27.5	53.4	49.7	49.4
	30.4	29.9	28.6	44.5	68.2	68.6	67.4
Metaperiodate	23.3	22.8	21.4	18.7	39.1	35.3	—
	27.6	26.8	25.6	35.5	57.6	54.2	57.9
	31.8	31.0	29.0	52.4	72.4	73.0	—
Hydrochloric acid	17.2	18.9	18.2	22.5	24.6	22.0	23.2
	25.4	26.6	26.4	57.5	59.8	60.3	—
Alkaline hypobromite	17.1	22.3	19.2	24.0	37.3	28.7	27.3
	26.4	29.7	27.4	60.5	65.7	65.3	—
Alkaline hypochlorite	18.5	21.0	20.0	24.6	31.0	27.9	27.0
	23.5	27.1	25.7	46.6	58.8	51.7	—
Neutral hypochlorite	11.7	18.8	17.3	21.4	26.8	27.7	29.4
	22.8	29.6	29.3	60.1	67.3	66.9	—
Acid hypochlorite	9.4	19.4	18.5	25.2	36.6	29.9	32.4
	15.9	27.6	27.7	53.1	61.5	62.2	—
Dichromate and sulphuric acid	19.9	23.8	22.2	28.0	41.1	36.0	36.6
	25.4	29.0	27.9	56.1	64.9	62.4	—
Dichromate and oxalic acid	19.9	23.3	20.6	25.6	44.4	33.6	33.0
	23.5	26.2	24.8	39.3	59.2	49.0	—

Pre-treatment A—0.25*N* NaOH, 126°C, 6 hours

" B—0.1*N* NaOH, 20°C, 24 hours

" C—2.5*N* NaOH, 15°C, 24 hours

With the hydrocelluloses small rises in fluidity and solubility are observed as a result of both treatments, and with the alkaline hypochlorite, alkaline hypobromite and dichromate series of oxycelluloses somewhat greater rises in both properties occur. The effect of the alkaline treatments on the acid and neutral hypochlorite oxycelluloses is to produce large rises in fluidity and relatively small rises in solubility, while with the periodate oxycelluloses there are small decreases in fluidity accompanied by large increases in solubility.

It is at first sight surprising that pre-treatment with 0.1*N* sodium hydroxide at 20°C should produce any effect on the solubility of modified

cottons in 2.5*N* sodium hydroxide solution, and in particular that it should produce the large increases of solubility shown by the periodate oxycelluloses. It is to be recalled, however, that in the standard technique used in the measurement of solubility the modified cotton is in contact with the alkali at the much lower temperature of  $-5^{\circ}\text{C}.$ , except for an initial short period of mixing at  $15^{\circ}\text{C}.$  If the standard technique is altered so that the duration of the initial mixing stage is increased to 24 hours ("Pre-treatment C" in Table I), the solubility so measured is then not very different from that obtained by the standard method applied to the same material pre-treated with 0.1*N* sodium hydroxide for 24 hours at  $20^{\circ}\text{C}.$  ("Pre-treatment B" in Table I). The increase in solubility produced by the prolonged steeping of the modified cottons in 2.5*N* sodium hydroxide solution at  $15^{\circ}\text{C}.$  is much greater with the periodate oxycelluloses than with the other modified cottons, and this result shows that treatment which with these latter types is adequate for the realization of the full potential solubility is inadequate with the periodate oxycelluloses.

The solubility of a modified cotton has been interpreted as a measure of the proportion of the material that consists of chain-molecules shorter than a certain length, this critical length being dependent on the conditions employed in the solubility measurement.<sup>1</sup> Oxycelluloses of the reducing type are believed to contain in their chain-molecules linkages that may be broken by the action of alkalis,<sup>2,3</sup> and with such materials it is clear that the solubility will be determined not by the frequency distribution of chain-length in the original oxycelluloses, but by the distribution as modified by the rupture of alkali-sensitive linkages during the determination of solubility. Since fluidity in cuprammonium solution is also a function of the frequency distribution of chain-length, a functional relation between fluidity and solubility is to be expected within any one series of modified cottons. This relation will be the same for different methods of modification only if the distribution of breaks in the chain-molecules (including potential breaks due to alkali-sensitive linkages) changes in the same way with progressive attack by all kinds of chemical agents, and if sodium hydroxide under the conditions of the solubility measurement and cuprammonium under the conditions of the fluidity measurement are equally effective in breaking the alkali-sensitive linkages. The fact that the same relation between fluidity and solubility is given by the types of modified cotton that contain no alkali-sensitive linkages (hydrocelluloses, alkaline hypobromite and alkaline hypochlorite oxycelluloses) and by all types after adequate pre-treatment with cold dilute sodium hydroxide suggests that the first condition is fulfilled, and the abnormal fluidity-solubility relation shown by the periodate, neutral hypochlorite and acid hypochlorite oxycelluloses before this treatment may be explained by the assumption that the second condition is not satisfied. The results given in Table I suggest that sodium hydroxide under the conditions of the solubility determination is not able to break all the linkages in periodate oxycelluloses that may be broken by a more prolonged treatment with the same alkali, and the abnormally low solubility of these products when compared with hydrocelluloses of equal fluidity would be accounted for if alkali-sensitive linkages not broken in the solubility measurement were broken by cuprammonium in the fluidity measurement. The abnormal behaviour of the periodate oxycelluloses when compared with other types of reducing oxycelluloses may be due to the presence of a greater

proportion of alkali-sensitive linkages, or it may be due to a difference in chemical nature between such linkages in periodate oxycelluloses and other alkali-sensitive products. The neutral and acid hypochlorite oxycelluloses are exceptional in showing an abnormally great rise of fluidity as a result of treatment with dilute sodium hydroxide, and this must be interpreted to mean that with these types of oxycelluloses cuprammonium is not able to break all the linkages that may be broken by sodium hydroxide. The abnormally high solubility of the neutral and acid hypochlorite oxycelluloses when compared with hydrocelluloses of equal fluidity must therefore be regarded as a consequence of their abnormal behaviour towards cuprammonium.

The observation that after alkali-boiling the relation between fluidity and solubility is the same whatever the method of modification could not have been predicted in view of the unpredictable changes in the frequency distribution of chain-length arising from the widely different losses in weight suffered by the various types of modified cotton on alkali-boiling.

### EXPERIMENTAL

#### Materials and Methods

The modified cottons employed were the hydro- and oxy-celluloses derived from cotton linters that were used in two earlier investigations; details of their preparation have already been given <sup>2, 3</sup>

Fluidity in cuprammonium solution was determined by the method of Clibbens and Geake <sup>4, 5, 6</sup>. The values recorded are the fluidities in c g s. units of 0.5 per cent. cellulose solutions at 20° C.

Solubility in 2.5*N* sodium hydroxide solution at -5° C was measured according to the general procedure described in Part 2 of this series,<sup>7</sup> except that in the determination of the dissolved cellulose by oxidation with chromic acid the "redox" indicator employed was phenylanthranilic acid.

#### Results

The fluidity and solubility data for the various types of modified cotton, and for the same materials after boiling for six hours with 0.25*N* sodium hydroxide solution under a pressure 20 lb per sq inch in excess of atmospheric (126° C.), are given in Table II, and the relations between the two properties are illustrated in Figs. 1A, 1B and 2.

The effects of pre-treatment of the modified cottons with 0.1*N* sodium hydroxide for 24 hours at 20° C and with 2.5*N* sodium hydroxide for 24 hours at 15° C have already been given in Table I, where they are compared with the effects of boiling with 0.25*N* sodium hydroxide under pressure.

### SUMMARY

The effect of the method of modification on the relation between the fluidity in cuprammonium solution of chemically modified cotton celluloses and their fractional solubility in 2.5*N* sodium hydroxide solution at -5° C. has been investigated. Oxycelluloses prepared by the action of alkaline hypobromite or alkaline hypochlorite, or of dichromate in the presence of sulphuric or oxalic acid, give approximately the same fluidity-solubility relation as hydrocelluloses, but neutral hypochlorite and acid hypochlorite oxycelluloses are considerably more soluble, and periodic acid and meta-periodate oxycelluloses considerably less soluble, than hydrocelluloses of equal fluidity. Treatment of the modified cottons with cold or hot dilute sodium hydroxide solution produces changes of fluidity and solubility that

**Table II**  
**Fluidity in Cuprammonium Solution and Solubility in**  
**2.5N Sodium Hydroxide Solution at  $-5^{\circ}\text{C}$ .**

BEFORE ALKALI-BOILING		AFTER ALKALI-BOILING		BEFORE ALKALI-BOILING		AFTER ALKALI-BOILING	
Fluidity	% dissolved	Fluidity	% dissolved	Fluidity	% dissolved	Fluidity	% dissolved
<i>Linters —</i>				<i>Modified by acid hypochlorite —</i>			
5.6	4.3	6.8	5.7	7.5	10.9	12.5	16.2
				8.8	12.1	14.6	18.6
				9.4	25.2	19.4	36.6
<i>Modified by hydrochloric acid —</i>				10.3	29.7	20.6	37.2
12.8	10.4	14.2	15.6	11.0	30.7	21.5	43.1
17.2	22.5	18.9	24.6	12.0	42.4	25.3	53.6
22.4	41.2	23.5	46.0	15.9	53.1	27.6	61.5
25.4	57.5	26.6	59.8	16.8	64.9	30.3	76.3
27.0	60.2	27.8	65.7	20.3	74.9	34.6	84.8
27.6	63.7	28.7	66.7	23.3	84.8	36.9	90.8
31.1	73.6	32.0	74.1	27.2	92.0	40.0	96.0
34.8	84.5	35.6	88.5	30.2	94.7	42.0	97.8
36.9	88.8	37.1	89.0	<i>Modified by dichromate in sulphuric acid solution —</i>			
38.8	94.1	39.2	96.8	10.6	7.5	13.5	10.7
41.5	96.8	—	—	15.4	14.3	19.1	23.6
<i>Modified by alkaline hypobromite —</i>				19.9	28.0	23.8	41.1
11.8	10.6	15.8	15.8	25.2	52.3	29.4	61.8
17.1	24.0	22.3	37.3	25.4	56.1	29.0	64.9
22.5	44.3	27.0	58.3	26.3	63.9	29.9	70.8
26.4	60.5	29.7	65.7	31.0	82.3	34.6	86.2
27.4	63.5	31.1	71.5	32.5	85.3	37.0	85.1
29.8	75.6	34.2	82.7	36.4	91.7	40.0	92.3
35.0	88.3	37.7	90.0	39.4	95.7	42.8	93.2
40.6	95.1	43.0	96.4	42.9	96.9	44.8	95.1
<i>Modified by alkaline hypochlorite —</i>				<i>Modified by dichromate in oxalic acid solution —</i>			
11.6	9.4	13.9	12.6	12.0	10.3	14.9	17.2
18.5	24.0	21.0	31.0	15.2	13.7	17.9	26.3
21.5	31.3	24.1	43.8	19.9	25.6	23.3	44.4
22.9	40.3	26.7	50.7	23.5	39.3	26.2	59.2
23.5	46.6	27.1	58.8	28.4	58.6	30.2	73.0
23.9	46.5	26.5	53.5	32.5	75.2	34.2	83.1
26.7	57.2	30.1	70.8	37.2	86.5	38.1	94.9
29.9	72.3	33.1	81.9	<i>Modified by periodic acid —</i>			
33.4	85.5	36.0	88.0	14.6	8.4	14.8	16.2
35.5	90.6	36.8	92.3	19.1	13.7	19.0	27.6
38.0	95.5	39.8	95.0	20.4	14.1	20.0	26.8
<i>Modified by neutral hypochlorite —</i>				26.0	27.1	25.1	50.4
11.7	21.4	18.8	26.8	26.5	27.5	25.7	53.4
13.7	29.6	22.9	44.3	30.4	44.5	29.9	68.2
14.0	30.2	20.9	38.0	32.9	54.5	31.0	81.4
20.9	53.0	29.8	69.1	34.8	63.5	33.5	79.2
22.8	60.1	29.6	67.3	38.3	79.9	36.8	89.5
25.0	69.4	33.0	79.8	38.5	78.1	36.9	92.8
29.5	78.8	36.0	85.2	41.6	87.5	39.7	97.1
33.8	88.7	37.6	89.0	<i>Modified by metaperiodate —</i>			
36.0	91.6	39.7	95.6	16.3	10.0	16.6	18.4
36.7	91.5	40.0	94.5	19.5	12.6	19.4	23.0
41.4	94.9	42.5	95.0	23.3	18.7	22.8	39.1
				27.6	35.5	26.8	57.6
				31.8	52.4	31.0	72.4
				36.9	74.7	35.2	85.2

vary in magnitude from one type of modified cotton to another, and after these treatments the relation between the two properties is the same whatever the method of modification. Periodic acid and metaperiodate oxycelluloses are exceptional in showing relatively large increases of solubility as a result of pre-treatment with cold dilute sodium hydroxide solution, and this behaviour is ascribed to the presence in these oxycelluloses of alkali-sensitive linkages that are not broken by the relatively short alkali treatment involved in the solubility measurement. The abnormal fluidity-solubility relation given by the neutral hypochlorite and acid hypochlorite oxycelluloses is due mainly to an abnormality in the behaviour of these types of modified cotton towards cuprammonium.

## REFERENCES

- <sup>1</sup>Davidson *Shirley Inst Mem*, 1934, 13, 1, or *J Text Inst*, 1934, 25, 1174.
- <sup>2</sup>Davidson *Shirley Inst Mem*, 1939-40, 17, 83, or *J Text Inst*, 1940, 31, 181.
- <sup>3</sup>Davidson *Shirley Inst Mem*, 1937-38, 16, 29, or *J Text Inst*, 1938, 29, 1195.
- <sup>4</sup>Clibbens and Geake *Shirley Inst Mem*, 1927, 6, 117, or *J Text Inst*, 1928, 19, 177.
- <sup>5</sup>Department of Scientific and Industrial Research, Fabrics Co-ordinating Research Committee "The Viscosity of Cellulose Solutions," H M Stationery Office, London, 1932.
- <sup>6</sup>Clibbens and Little *Shirley Inst Mem*, 1936, 15, 25, or *J. Text Inst*, 1936, 27, 1285.
- <sup>7</sup>Davidson. *Shirley Inst Mem*, 1935, 14, 43, or *J Text. Inst*, 1936, 27, 1112.

Received 15/1/41



#### 4—THE DISSOLUTION OF CHEMICALLY MODIFIED COTTON CELLULOSE IN ALKALINE SOLUTIONS.

##### PART VII. THE SOLVENT ACTION OF SOLUTIONS OF TRIMETHYLBENZYL- AND DIMETHYLDIBENZYL-AMMONIUM HYDROXIDES (TRITONS B AND F).

By T. BROWNETT and D. A. CLIBBENS.

(The British Cotton Industry Research Association)

(Copyright by The Textile Institute)

Previous papers published from these laboratories contain measurements and discussions concerned with the partial solubility of chemically modified cotton celluloses in solutions of lithium, sodium, potassium, and tetramethylammonium hydroxides, and in cuprammonium and cupri-ethylene-diamine solutions, at 15° C. and lower temperatures (Davidson,<sup>1</sup> Jolley,<sup>2</sup> Brownsett and Davidson<sup>3</sup>) The "Solubility" or "Fractional Solubility" of a modified cellulose is defined as the proportion of the material that dissolves in the alkali, expressed as a percentage of the total weight of cellulose in the system Davidson has shown that this quantity acquires a theoretical significance when the modified celluloses are regarded as heterogeneous in respect to the length of the chain-molecules, and that it describes a feature of the chain-length frequency distribution The relations studied experimentally were those between solubility and concentration of the alkali, temperature, and degree of chemical modification of the cellulose as measured by the fluidity of its 0.5 per cent. solution in cuprammonium Other factors, the influence of which must be associated with the very imperfect reversibility of cellulose swelling, were also found to affect the solubility. The exact temperature path by which the system is brought to the temperature of investigation, and the history of the cellulose in respect to swelling treatment prior to its swelling in the solvent alkali are factors of this kind.

Solutions of certain quaternary ammonium hydroxides are better solvents for cellulose than the tetramethyl base, or the hydroxides of the alkali metals, as shown by the semi-quantitative observations recorded by Lieser for bases in which one or more of the methyl groups in tetramethylammonium hydroxide are replaced by ethyl, propyl, butyl, and tolyl groups.<sup>4, 5</sup> The use of benzyl-substituted ammonium hydroxides as cellulose solvents was patented recently,<sup>6</sup> and solutions of trimethylbenzyl- and dimethyldibenzyl-ammonium hydroxides became commercially available under the names of Triton B and Triton F, respectively. The methods used in these laboratories for other bases have now been applied in a study of cellulose solubility in the Tritons, and the results are compared with those previously obtained for tetramethylammonium hydroxide and the hydroxides of the alkali metals

The solutions of trimethylbenzyl- and dimethyldibenzyl-ammonium hydroxides employed were obtained by the dilution, or concentration, of the commercial liquids without purification These are not chemically pure solutions of the bases, and solutions of the dibenzyl derivative of different delivery dates varied appreciably in solvent and other properties at a constant concentration of titratable base, the results to be illustrated in the figures were all obtained with the same commercial sample unless otherwise stated.

**Solubility in Trimethylbenzylammonium Hydroxide (Triton B)**

Fig. 1 shows the solubilities at 20° C. of three samples of cotton cellulose in trimethylbenzylammonium hydroxide solutions of various concentrations between 1.5 and 4.0*N*. The samples differ in extent of cellulose modification as described by cuprammonium fluidities (0.5 per cent. solutions at 20° C.) of 5.6, 17.2 and 34.1. The first of these is, in a technical sense, an unmodified cotton cellulose, having suffered no more chemical degradation than is incidental to a carefully conducted bleaching operation, and no significant loss in tensile strength. The last is considerably modified so that, whilst still retaining the fibre structure, it would be expected to retain only about one quarter of the original fibre strength.

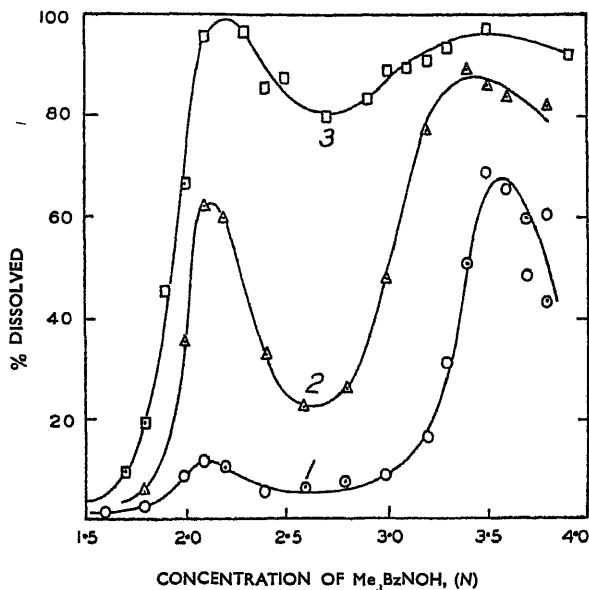


Fig. 1

Fractional solubility of modified cottons in trimethylbenzylammonium hydroxide at 20° C. (1) Fluidity 5.6, (2) Fluidity 17.2; (3) Fluidity 34.1.

With each sample the solubility attains a maximum in a 2.15*N* solution of the base at 20° C., and in this region small changes in the concentration may result in large solubility changes, the solubility at a given concentration of base increases with the extent of cellulose modification. Solubility curves obtained with other strong bases already investigated show similar maxima to those occurring at a concentration of 2.15*N* in Fig. 1, though the concentration for maximum solubility in trimethylbenzylammonium hydroxide is lower than that in any alkali previously investigated (NaOH. 3.0*N*, LiOH 3.3*N*, KOH ca 3*N*, Me<sub>4</sub>NOH: 2.5*N*\*).

At higher concentrations of the base the solubility falls to a minimum and rises to a second maximum at a concentration of about 3.5*N*. In previous papers it was shown that a second solubility maximum occurs also with potassium and tetramethylammonium hydroxides, but not with sodium

\* Earlier investigations with other alkalis were made at 15° C., instead of, as now, at 20° C., but the effect of this temperature difference on the position of the maximum is very small.

and lithium hydroxides, in which the cellulose solubility continued to fall up to the highest concentrations investigated. In concentrations of the quaternary ammonium base above that of the first maximum, cotton cellulose forms highly swollen gels, and equilibrium between the phases is slow and difficult of attainment. On this account the points at the highest concentrations in Fig 1 show considerable scatter, and in the case of the unmodified cotton are only of qualitative value. Contributory causes of the slow attainment of equilibrium are the high absolute viscosities of the solutions of the base itself, the high relative viscosities of the cellulose solutions, and the desirability of agitating the mixture in the absence of air, which leads to a sacrifice either of simplicity in technique or of efficiency in

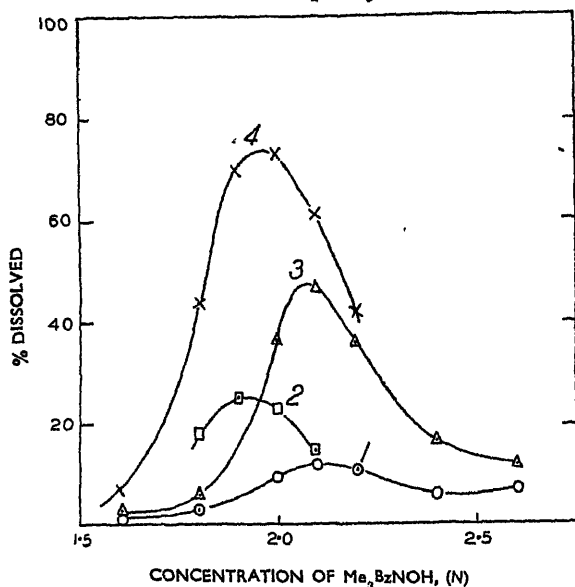


Fig. 2

Fractional solubility of modified cottons in trimethylbenzylammonium hydroxide

(1) Fluidity	5.6.	Temperature	20° C.
(2) "	5.6	"	0° C.
(3) "	14.2.	"	15° C.
(4) "	14.2.	"	0° C.

mixing. Of the three samples of cotton for which results are illustrated, only the most highly modified attains virtually complete solubility, and this it does in the neighbourhood of both concentrated optima.

Fig 2 shows the effect of lowering the temperature from 20° or 15° C to 0° C. on the solubility of two samples of cotton of fluidity 5.6 and 14.2. The difficulty of attaining equilibrium with the more concentrated solutions of the base at the lower temperature is still greater than at 15° C., and the course of the solubility curves has therefore only been determined up to concentrations a little beyond that of the first maximum. As with other alkalis, the concentration corresponding to maximum solubility decreases, and the solubility at the maximum increases, with fall of temperature.

#### Solubility in Dimethyldibenzylammonium Hydroxide (Triton F)

Fig. 3 shows the solubility of an unmodified cotton (Fluidity 5.6) and a slightly modified cotton (Fluidity 17.2) in dimethyldibenzylammonium hydroxide solutions of different concentrations at 20° C. and 0° C.

The curve for the unmodified cotton at 20° C. contains a maximum at a base concentration of 1.95*N*, but different commercial deliveries of the base differed in respect to the position of this maximum, which occurred at a concentration as low as 1.8*N* with one delivery. A real second maximum, in the neighbourhood of 2.5*N*, is almost certainly present in this curve, though the difficulty of ensuring true equilibrium prevents very precise solubility measurements at the higher concentrations. The modified cotton is almost completely soluble at 20° C in all concentrations investigated above about 1.9*N*. As with other bases examined, decrease of temperature displaces the solubility curves in the direction of lower concentrations.

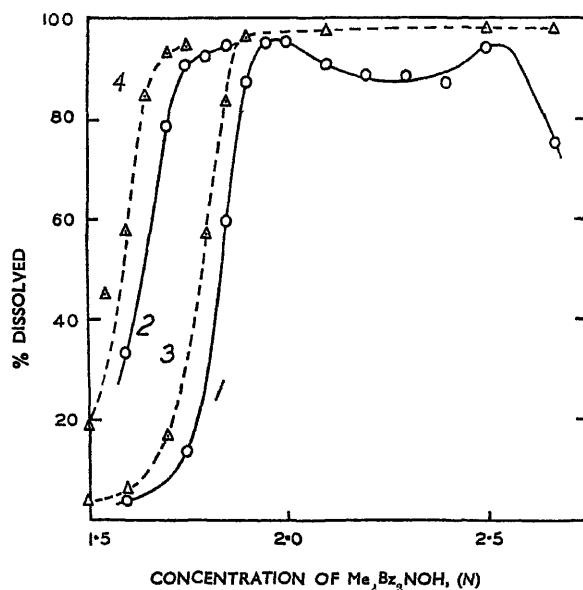


Fig. 3

Fractional solubility of modified cottons in dimethyldibenzylammonium hydroxide

(1)	Fluidity	5.6	Temperature	20° C
(2)	"	5.6	"	0° C.
(3)	"	17.2	"	20° C.
(4)	"	17.2	"	0° C.

The dibenzyl base is the best cellulose solvent among the non-complex bases studied in this series of investigations. It permits complete dissolution of an unmodified cotton at 20° C, and the maximum in the solubility curve occurs at the lowest normal concentration. Solutions of unmodified cotton in dimethyldibenzylammonium hydroxide can be diluted without precipitation of the cellulose even though the concentration of the base is thereby reduced to a value at which the solubility of the cotton determined by direct extraction is practically zero. Thus, when a 1 per cent solution of cotton in 2*N* base was diluted to twice its bulk, or a 0.75 per cent solution to four times its bulk, no precipitation occurred from the diluted solutions on long standing. Precipitation occurred, however, when the concentration of the base was reduced by dilution much below 0.5*N*, more rapidly the greater the dilution, and solutions in which precipitation had occurred were practically free from cellulose after several days' standing. A qualitatively similar behaviour has been recorded by Davidson for solutions of modified cotton in sodium hydroxide.

### Comparison of the Solvent Powers of Different Bases

The solubility of modified cotton cellulose in a strong base of a defined concentration and temperature increases with the fluidity (degree of chemical modification) of the cellulose. For a series of products modified by acid attack, Curve 2 in Fig. 4 shows, for example, the relation between the fluidity of the modified cotton and its solubility at 20° C. in the optimum concentration of trimethylbenzylammonium hydroxide. Similar curves for other bases, constructed from data in this or earlier papers, are included in the figure, and they arrange the six bases in the following order of decreasing solvent power at the ordinary temperature: Dimethyldibenzylammonium, trimethylbenzylammonium, tetramethylammonium, sodium, lithium, and

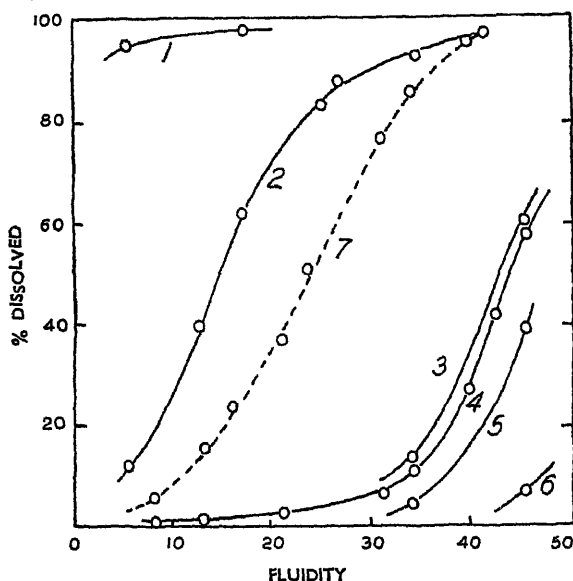


Fig. 4

Relation between fluidity of modified cottons and their fractional solubility in different bases at their optimum concentrations.

- (1) Dimethyldibenzylammonium hydroxide at 20°C.
- (2) Trimethylbenzylammonium hydroxide at 20°C.
- (3) Tetramethylammonium hydroxide at 15°C.
- (4) Sodium hydroxide at 15°C.
- (5) Lithium hydroxide at 15°C.
- (6) Potassium hydroxide at 15°C.
- (7) Sodium hydroxide at -5°C.

potassium hydroxide. The measurements were made at 20° C. for the Tritons, and at 15° C. for the other bases, but this temperature difference does not affect the order. The broken curve refers to sodium hydroxide at -5° C., and its solvent power under these conditions is seen to be only slightly inferior to that of trimethylbenzylammonium hydroxide at 20° C.

Curves such as those in Fig. 4 provide the best method at present available for comparing the solvent powers of different alkalis, but in view of the imperfect theoretical understanding of the solubility relations the basis of comparison remains an arbitrary one. Each curve relates to a different concentration of base, namely, to that of the maximum in the solubility curve—the first maximum when two exist. The effect of factors that presumably determine irreversible features of the swelling process has not been closely studied except for sodium and potassium hydroxides, but their

importance is such that the quantitative solubility data must be understood to relate to a closely prescribed laboratory technique applied to the treatment of a definite class of cellulose materials. The modified celluloses were all derived from native cotton cellulose that had received no swelling treatment either prior, or incidental, to its chemical modification. Different quantitative results would be obtained for "regenerated" celluloses, for modified celluloses made from mercerised cotton, or for modified celluloses made from cotton by the chemical action of an oxidising agent in the presence of alkali hydroxide of swelling concentration. Subject to these restrictions, the solubility is not greatly affected by the conditions of chemical modification provided that materials oxidised in neutral or acid solution receive a pre-treatment with dilute alkali to destroy alkali-sensitive links in the chain-molecule.<sup>3</sup>

#### **Comparison of the Solvent Powers with the Viscosities of different Bases**

An intimate relation exists between the swelling and the solubility of cellulose in strong bases, explained by Davidson in the following way. The dissolved fraction consists of all the chain-molecules below a certain limiting length determined by the degree of swelling, and the greater the swelling the greater is this upper limit to the length of the soluble chain-molecules. Thus, solubility is determined in general both by degree of swelling and the molecular chain-length distribution of the cellulose, but for a given cellulose it is a function of swelling only. No general relation has, however, been found between their swelling or solvent action and any other property of the strong bases.

Lieser<sup>4, 5</sup> compared the solvent actions of a considerable number of strong organic bases by determining the minimum molar concentration necessary to effect complete dissolution of a certain cellulose preparation. He observed that in the group of quaternary ammonium hydroxides this minimum concentration decreases as the molecular weight of the base increases, though no such relation obtains for the generality of strong bases. The swelling and dissolution of the cellulose are accompanied by the formation of a compound between the cellulose and the base, which possesses an X-ray diagram different from that of the native or regenerated cellulose. The X-ray diagrams of cellulose fibres swollen in tetramethyl-, trimethylethyl-, trimethylbenzyl-, and dimethyldibenzyl-ammonium hydroxides were studied by Sisson and Saner,<sup>7</sup> who observed that the minimum molar concentration necessary to produce the "alkali-cellulose" X-ray diagram decreases as the molecular weight of the base increases in this series of quaternary ammonium hydroxides. To this extent the results obtained by Sisson and Saner run parallel to those recorded by Lieser, who sought to explain his observations on the hypothesis that the swelling and dissolution of the cellulose are due to the introduction of a large molecule between the cellulose chains. According to this view, solvent action increases with the molecular volume of the solvated base, of which the molecular weight affords a measure among the closely related substances comprising the group of quaternary ammonium hydroxides. The X-ray analysis shows that the formation of the alkali-cellulose is accompanied by an extension of the lattice in the crystalline zones of the cellulose fibre, but there is, however, no significant difference in this respect between trimethylbenzyl- and dimethyldibenzyl-ammonium hydroxides, in spite of the large difference in molecular weight and solvent action of the two bases.

In view of the suggested relation between cellulose dissolving power and the molecular volume of the solvated base, it is of interest to compare the order of solvent power of the six bases to which Fig 4 refers with the order of the viscosity of these substances in equivalent aqueous solutions. Fig 5 shows the relative viscosities at 20° C (water = 1) of solutions of the bases of various concentrations, the data plotted being the results of new measurements except those for potassium hydroxide. The two different curves (1A and 1B) given for the dibenzyl-substituted quaternary base were obtained from two different deliveries of Triton F.

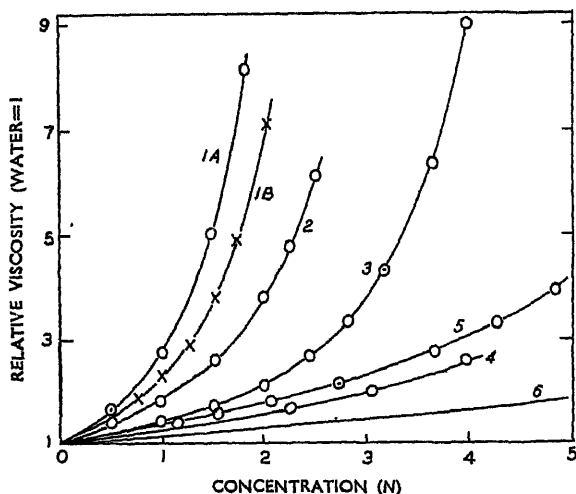


Fig. 5

Relative viscosities of aqueous solutions of different bases at 20° C.

- (1) Dimethyldibenzylammonium hydroxide (deliveries A and B).
- (2) Trimethylbenzylammonium hydroxide.
- (3) Tetramethylammonium hydroxide.
- (4) Sodium hydroxide.
- (5) Lithium hydroxide.
- (6) Potassium hydroxide.

Comparison of Figs 4 and 5 shows that, except for sodium and lithium hydroxides, there is qualitative agreement between the order of solvent power and of viscosity at a given normal concentration, the more viscous bases being the better solvents, this relation is also valid for the two samples of Triton F in the sense that the maximum in the solubility curve was attained at a lower concentration with the more, than with the less, viscous sample.

#### EXPERIMENTAL

##### (1) Modified and Unmodified Cottons

The samples of cotton used were (a) An unmodified cotton linters, No 327, mechanically cleaned, scoured by boiling under pressure with 2 per cent sodium hydroxide solution, and lightly bleached. The fluidity of its 0.5 per cent solution in cuprammonium at 20° C. was 5.6. (b) Three modified cottons, HL8B, HL9 and OL7B, prepared from purified linters, of fluidity 14.2, 17.2 and 34.1 respectively. The first two were hydrocelluloses made by the action of hydrochloric acid, 200 gm per l., at the room temperature, and the third was an oxycellulose prepared with *N*/5 sodium hypochlorite solution, pH 8.4, also at room temperature. The first and third were boiled with dilute sodium hydroxide solution following the

chemical modification. (c) A series of hydrocelluloses HL8 to 14 prepared as above and covering a fluidity range from 12 to 40

## (2) Solvents

**Tritons.** Supplies of the Tritons were obtained through the courtesy of Mr D H. Powers of the Rohm & Haas Co. (U.S.A.). For the work described here, two different deliveries of each base were used, and these will be referred to as Solution A and Solution B. Both samples of Triton B were 2.5*N* in titratable alkali, whilst those of Triton F were 1.8*N* and 2.0*N*. All the solutions were free from sulphate ion, but contained chloride and carbonate ions in low concentrations. The equivalent ratio of chloride to hydroxyl ion was below 0.01 for Triton B and below 0.05 for Triton F, the corresponding limits for the equivalent ratio of carbonate to hydroxyl ion were 0.005 and 0.025. Known weights of the solutions, when evaporated and ignited, yielded inorganic residues weighing 0.03 gm and 0.17 gm per 100 gm of Triton B and Triton F solutions respectively. Electrometric titrations of the original solutions gave simple strong-base curves, and yielded no evidence of the presence of weak bases such as the tertiary amines. Solutions more concentrated than the originals were obtained by evaporation at 40°C under reduced pressure, and the concentrated solutions contained no weak bases detectable by electrometric titration.

Weighed samples of Triton B and Triton F were exactly neutralised with sulphuric acid, evaporated to dryness, and the residues dried over phosphorus pentoxide and weighed. The following are the results obtained expressed as the percentage differences from the weights calculated on the assumptions that the titratable base consisted entirely of  $\text{Me}_2\text{BzNOH}$  or  $\text{Me}_2\text{Bz}_2\text{NOH}$ , and that the dried residues were the anhydrous sulphates of these bases

	Solution A	Solution B
Triton B ... ..	+1.3%	+1.3%
Triton F . . . . .	-4.8%	-11.8%

The results for Triton B are higher, those for Triton F lower, than the theoretical, and this would be explained if Triton B contained a small amount of the dibenzyl base, Triton F a small amount of the monobenzyl base. The low "ash" content already recorded shows that the deficiency for Triton F in the above analyses cannot be ascribed to contamination with an alkali metal hydroxide. The two solutions of Triton B yield the same result, but for Triton F, Solution B diverges more from the theoretical than Solution A. As will be seen from the tables of results, the two solutions of Triton F also differed significantly in viscosity, density and cellulose dissolving power, no such difference existed between the two solutions of Triton B.

**Tetramethylammonium hydroxide** The base was made by shaking a solution of its chloride with freshly precipitated silver oxide, filtering off the silver chloride, concentrating the solution in vacuo to crystallisation, and purifying the base by recrystallisation from water. The purified material contained traces of chloride and nitrate, the equivalent ratio of these two ions to the hydroxide being about 0.008 for both.

**Alkali metal hydroxides** Solutions of sodium hydroxide were made by dilution from a nearly saturated solution of a laboratory reagent quality, and were free from carbonate. Solutions of lithium hydroxide were also made from a laboratory reagent grade, and were free from carbonate. Two recrystallisations of this material from water were without effect on the viscosity of solutions of a given normality.



### (3) Determination of Solubility

Previous work has shown the advisability of a strictly standardised technique for the solubility measurement, in which the modified cotton is brought in contact with alkali of the concentration under investigation, and at a defined temperature subsequently adjusted to the desired value. If the cotton is brought in contact with alkali at a different concentration from that under investigation, or at a different temperature from that arbitrarily defined, and these variables are subsequently adjusted to the desired values, the measured solubility may differ considerably from that obtained by the standard procedure.

In all determinations of the solubility of cotton in the Tritons the ratio of cellulose to solution was 0.5 gm. to 100 c.c. The solvent at the desired concentration was first brought to a temperature of 15° C., mixed with the cotton, and then the system brought to the temperature at which the observations were to be made.

(a) *Method of dissolution* For the experiments at 15° C and 20° C. the dissolution vessel was a glass tube about 20 cm long and 1.5 cm. diameter, of known volume (about 20 c.c.), sealed at one end, and closed at the other with a glass capillary stopper secured by horns and rubber bands. The tube was nearly filled with solvent, the necessary weight of cotton introduced, together with a  $\frac{3}{8}$  inch steel ball, the mixture stirred to dislodge air bubbles, and the tube then completely filled with the solvent. The stopper was inserted, the excess liquid being expressed through the capillary, which was then closed. The tube was fastened to a slowly rotating wheel in an air thermostat at the required temperature so that it received an end-over-end motion, and the agitation of the contents was produced by the resulting to-and-fro motion of the steel ball. After times of agitation up to 24 hours, the contents of the tube were transferred to a vessel in which they could be centrifuged for about 10 minutes, and 10 c.c. of the clear liquid was taken for cellulose determination.

For the experiments at 0° C the dissolution vessel was a glass stoppered centrifuge tube. The mixture of cotton and solvent was stood in melting ice for six hours, being occasionally shaken by hand. It was then allowed to attain room temperature, centrifuged, and a 10 c.c. sample of the clear liquid taken for analysis. The method proved adequate for the attainment of equilibrium provided the concentration of the base was not too high.

It will be seen that the dissolution at 15° or 20° C was conducted in the absence of air, but not that at 0° C. This was done primarily to suit experimental convenience, but the risk of serious error due to oxidation of the cellulose by the air is obviously greater at the higher temperature.

(b) *Cellulose determination* Dissolved cellulose was determined volumetrically as usual by wet combustion with chromic acid. It was necessary first to separate the cellulose from its solution since the oxidising agent is not perfectly stable in the presence of the Triton bases alone under the combustion conditions. In a centrifuge tube, 10 c.c. of the cellulose solution was acidified with 3*N* sulphuric acid, the precipitated cellulose was centrifuged down, and the liquid decanted off through a fritted glass filter. The cellulose was washed by stirring with water, centrifuging, and decanting the washings through the filter until they were free from sulphate. The precipitate in the tube and on the filter was transferred quantitatively to the wet combustion flask by dissolving it in 75 per cent. sulphuric acid,

and the analysis conducted in the usual way by boiling with excess of *N* dichromate at a suitable concentration of acid. The excess of dichromate was determined by titration with 0.1*N* ferrous ammonium sulphate, phenylanthranilic acid being used as internal indicator.

The results obtained on pure cotton cellulose by the wet combustion method are generally 2 or 3 per cent. below the theoretical, so that a recorded solubility of 97 to 98 per cent corresponds to complete dissolution of the cotton.

#### (4) Viscometry

For the viscosity measurements, solutions of known concentration were made by weighing a suitable quantity of a more concentrated solution of pre-determined base content in a dry, weighed, measuring flask (50.00 c.c.), making up to volume at 20°C, and weighing again. From the figures obtained, the density and concentration of the solution were calculated. After the viscosity of the solution had been measured it was used for the next dilution in the series. The concentrations of some of the intermediate solutions, and of the last, in each series were determined as a check on the dilution, and on the carbonate content.

Viscosities were measured at  $20 \pm 0.05^\circ\text{C}$  in a suspended level viscometer as designed by Ubbelohde, with a constant of 0.01 centistokes per sec. and a kinetic energy correction of 2 per cent. at the maximum rate of flow for which observations were made.

Table I  
Solubility of Modified and Unmodified Cotton in Trimethylbenzylammonium Hydroxide (Triton B) at 20°, 15° and 0° C.

Concentration of base <i>N</i>	% Dissolved					
	Unmodified cotton No 327 (F=5.6)		Hydrocellulose HL8B (F=14.2)		Hydrocellulose HL9 (F=17.2)	Oxy-cellulose OL7B (F=34.1)
	at 20°C	at 0°C	at 15°C	at 0°C	at 20°C	at 20°C
1.5	—	—	—	—	—	3.73
1.6	1.25	—	1.54	6.60	—	—
1.7	—	—	—	—	—	9.39
1.8	2.30	17.52	5.60	43.7	5.56	19.10
1.9	—	24.9	—	69.3	—	45.7
2.0	8.87	22.2	36.0	72.4	34.8	66.2
2.1	11.70	13.9	46.4	60.3	61.0	95.7
2.2	10.04	—	35.5	41.4	59.2	—
2.3	—	—	—	—	—	96.4
2.4	5.53	—	16.17	—	32.3	85.1
2.5	—	—	—	—	—	87.0
2.6	6.66	—	11.67	—	22.1	—
2.7	—	—	—	—	—	79.5
2.8	7.20	—	—	—	25.9	—
2.9	—	—	—	—	—	82.6
3.0	8.87	—	—	—	47.4	88.5
3.1	—	—	—	—	—	88.7
3.2	16.17	—	—	—	76.4	90.8
3.3	30.9	—	—	—	—	93.2
3.4	50.5	—	—	—	88.6	—
3.5	68.8	—	—	—	85.3	96.7
3.6	65.3	—	—	—	83.4	—
3.7	59.9, 48.4,	—	—	—	—	—
3.8	60.1, 43.1	—	—	—	81.4	—
3.9	—	—	—	—	—	91.9

## (5) Results

The results are contained in Tables I to IV. The solubility data with Triton B (Table I) have been graphed in Figs 1 and 2, and those obtained with the Solution B of Triton F (Table III) are illustrated in Fig. 3. The results in Table II are shown by Curve 2 in Fig. 4, Curves 3 to 7 in this figure being constructed from data recorded in previous papers of this series.

Table II

Solubility of Hydrocelluloses in 2.1*N*. Trimethylbenzylammonium Hydroxide (Triton B) at 20° C.

Sample No	HL8	HL9	HL10	HL11	HL12	HL14
Fluidity	12.8	17.2	25.4	27.0	34.8	41.4
% Dissolved	39.5	61.9	83.1	87.4	92.3	97.3

Table III

Solubility of Modified and Unmodified Cotton in Dimethyldibenzylammonium Hydroxide (Triton F) at 20° and 0° C.

Concentration of base <i>N</i>	% Dissolved					
	Unmodified cotton No. 327 (F=5.6)			Hydrocellulose HL9 (F=17.2)		
	at 20°C (Solution A)	at 20°C (Solution B)	at 0°C (Solution B)	at 20°C (Solution A)	at 20°C (Solution B)	at 0°C (Solution B)
1.50	—	—	—	—	3.56	18.5
1.60	5.67	3.97	33.0	11.80	5.67	57.5
1.65	—	—	—	—	—	84.6
1.70	26.6	—	78.7	56.2	16.7	93.6
1.75	56.4	13.2	90.8	81.4	—	94.7
1.80	88.9	—	92.3	97.2	57.0	—
1.83	95.7	—	—	—	—	—
1.85	—	59.3	94.6	—	83.8	—
1.90	—	87.2	94.4	—	96.5	—
1.95	—	95.0	94.2	—	—	—
2.00	93.9	95.4	—	—	—	—
2.10	—	90.8	—	—	97.7	—
2.20	74.5	88.5	—	—	—	—
2.30	—	88.4	—	—	—	—
2.40	84.6	86.9	—	94.5	—	—
2.50	—	94.1	—	—	98.2	—
2.67	—	75.5	—	—	98.2	—

The viscosity data (Table IV) are illustrated in Fig. 5. Those for sodium hydroxide serve principally as a check on the viscometry, and they agree well with the measurements of Hitchcock and McIlhenny,<sup>8</sup> and those of Faust.<sup>9</sup> The results obtained for the viscosity of lithium hydroxide solutions are in fair agreement with measurements reported by Briner, Tykociner and Alfimoff,<sup>10</sup> but are significantly higher than the values given by Faust.<sup>9</sup>

No measurements of the viscosity of potassium hydroxide have been made, the curve for this alkali in Fig. 5 being constructed from the results recorded by Hitchcock and McIlhenny.<sup>8</sup>

## SUMMARY

Fractional solubilities of chemically modified cotton celluloses have been measured in solutions of trimethylbenzyl- and dimethyldibenzylammonium hydroxides (Tritons B and F respectively). The solubility/concentration curves for these two bases at 20° C., like that for tetramethyl-

ammonium hydroxide, contain two maxima. The maximum solubility rises, and the concentration at which it occurs falls, when the temperature is lowered from 20° C. to 0° C. In this respect, the Tritons resemble all the other strong bases of which the cellulose solvent powers have been examined in this series of investigations. Triton F completely dissolves cotton cellulose in which the extent of chemical modification is no greater than that incidental to a careful chemical purification process ("unmodified cotton"). The first maximum in the solubility curve with Triton F occurs at a base concentration of about 1.9*N*, and this is lower than the normal concentration of maximum solvent power for any other base so far examined. A solution of unmodified cotton in Triton F can be diluted until the concentration of the base is as low as 0.5*N* without precipitation of the cellulose, though the solubility of cellulose in this concentration of Triton F determined by direct extraction is zero

Table IV  
Viscosities and Densities of Bases at 20° C.

Concentration ( <i>N</i> )	Density	Relative viscosity (Water = 1)	Concentration ( <i>N</i> )	Density	Relative viscosity (Water = 1)
<i>Tetramethylammonium hydroxide</i>			<i>Dimethyldibenzylammonium hydroxide</i> (Solution B)		
3.99	1.0360	8.97	2.019	1.0630	7.06
3.66	1.0315	6.29	1.730	1.0545	4.84
3.19	1.0260	4.24	1.509	1.0470	3.74
2.838	1.0210	3.28	1.257	1.0380	2.825
2.478	1.0175	2.61	0.993	1.0300	2.25
2.012	1.0125	2.035	0.750	1.0210	1.82
1.512	1.0085	1.625	0.498	1.0135	1.475
1.003	1.0040	1.34	0.255	1.0050	1.22
0.530	1.0010	1.15			
<i>Trimethylbenzylammonium hydroxide</i> (Solution A)			<i>Sodium hydroxide</i>		
2.471	1.0555	5.96	3.98	1.1510	2.54
1.922	1.0425	3.55	3.04	1.1185	1.99
0.989	1.0195	1.785	2.256	1.0890	1.645
<i>Trimethylbenzylammonium hydroxide</i> (Solution B)			<i>Lithium hydroxide</i>		
2.508	1.0580	6.04	4.85	1.1085	3.89
2.256	1.0505	4.70	4.28	1.0980	3.27
2.004	1.0445	3.73	3.67	1.0855	2.73
1.507	1.0320	2.515	2.753	1.0650	2.09
0.990	1.0200	1.78	2.090	1.0505	1.74
0.499	1.0085	1.325	1.558	1.0375	1.50
<i>Dimethyldibenzylammonium hydroxide</i> (Solution A)			1.164	1.0280	1.355
1.830	1.0670	8.06	1.015	1.0245	1.295
1.499	1.0550	4.93	0.487	1.0105	1.135
1.008	1.0360	2.67	<i>Lithium hydroxide (recrystallised)</i>		
0.490	1.0155	1.56	4.26	1.0965	3.24
			1.061	1.0255	1.32

At a given concentration of base, the solubility of modified cotton cellulose increases with the fluidity of its solution in cuprammonium, and the curve relating solubility at the optimum concentration to the fluidity of the cellulose affords the best measure at present available of the cellulose dissolving power of the base. By means of such curves, derived from measurements in this and previous papers, the solvent actions of six non-complex bases towards cellulose are compared at 20° C. or 15° C.

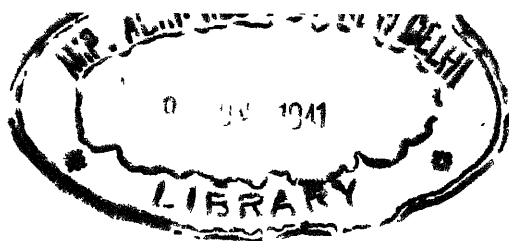
The viscosities of aqueous solutions of the same bases at 20° C. have been measured, and are recorded as functions of normal concentration. The

order of cellulose dissolving power is approximately the same as that of the viscosities of the bases, the best solvents being those that yield the most viscous solutions at a given normal concentration.

#### REFERENCES

- <sup>1</sup> Davidson *Shirley Inst Mem*, 1934, 13, 1, 1935, 14, 43, 1936, 15, 45, or *J Text. Inst*, 1934, 25, T174, 1936, 27, T112, 1937, 28, T27
- <sup>2</sup> Jolley *Shirley Inst Mem*, 1937-38, 16, 73 and 91, or *J Text Inst*, 1939, 40, T4 and T22
- <sup>3</sup> Brownsett and Davidson Foregoing paper
- <sup>4</sup> Lieser and Leckzych *Liebig's Ann Chem*, 1936, 522, 56
- <sup>5</sup> Lieser *Liebig's Ann Chem*, 1937, 528, 276
- <sup>6</sup> Powers, Bock and Houk U S P 2,009,015/1935 Rohm and Haas Co B P 455,253/1937
- <sup>7</sup> Sisson and Saner *J Phys Chem*, 1939, 43, 687.
- <sup>8</sup> Hitchcock and McIlhenny *Ind Eng Chem*, 1935, 27, 461.
- <sup>9</sup> Faust *Z anorg Chem*, 1927, 160, 373
- <sup>10</sup> Brner, Tykociner and Alfimoff *J Chim Phys*, 1920, 18, 3.

Received 15/1/41



# THE JOURNAL OF THE TEXTILE INSTITUTE

## TRANSACTIONS

### 5—COMPARATIVE OBSERVATIONS ON THE SWELLING OF JUTE FIBRE

#### 2—Specific Gravity and Swelling

By W G MACMILLAN, Ph D , F I C , and M K SEN, M Sc

*(Copyright by The Textile Institute)*

#### INTRODUCTION

It has been previously shown<sup>1</sup> that measurements of " diameter " by means of the microscope are unsuitable for the accurate determination of swelling in jute fibres. The extended investigation deals principally with specific gravity determinations, their utilisation in calculations relating to swelling and measurements on cross sections of jute fibres for the determination of swelling.

#### Specific Gravity.

Apart from its use for the determination of swelling, the specific gravity of jute fibre is, in itself, an important physical constant entering numerous calculations on fibre and yarn diameters, wetting, cover factor of fabrics and absorption and regain. Contributions regarding this physical property of fibres have been made by King<sup>2</sup> for wool, Peirce<sup>3</sup> and Clegg<sup>4</sup> for cotton, Matthew<sup>5</sup> and Preston<sup>6</sup> for flax, and Vignon<sup>7</sup> and Kubota<sup>8</sup>, and Goodings and Turl<sup>9</sup> for silk. The authors gratefully acknowledge the assistance received from the publications of these workers. The present technique for jute is largely based on their observations and methods.

The specific gravity of a solid, which neither absorbs nor is soluble in water, is equal to the weight of the substance in air divided by the weight of its own volume of water. The latter is given by the difference between the weight of water completely filling a specific gravity bottle and of the weight

of the water and substance filling it. Textile fibres, however, absorb water and swell. Since the volume of water absorbed is greater than the increase in volume of the fibre on swelling, a contraction in total volume must take place so that the resulting apparent specific gravity is appreciably greater than the true one. This difference will depend on the magnitudes of the absorption and the swelling. If, however, the fibres are saturated with water, and are therefore completely swollen before immersion, it is possible to obtain a true specific gravity using water as the medium. In all cases of incomplete saturation between absolute dryness and 100 per cent relative humidity, true specific gravities may be determined with the specific gravity bottle by immersion of the fibres in a non-swelling liquid.

The apparent specific gravity of incompletely saturated fibres in water will be a maximum when the amount of moisture present is zero, that is, when absolutely dry fibres are taken, and from this maximum value the apparent specific gravity corresponding to any regain may be calculated. If  $\Delta_a$  is the apparent specific gravity of dry fibre, the apparent specific gravity corresponding to  $w$  gms of moisture in  $\Delta_a$  gms of dry fibre is

$$\frac{\Delta_a + w}{1 + w}$$

Expressed in terms of regain  $R$  in 100 gms of dry fibre, the apparent specific gravity is given by

$$\Delta_R = \frac{100 + R}{\frac{100}{\Delta_a} + R} \dots \dots \dots 1$$

Provided  $\Delta_a$  is known, the expression may be utilised for estimating the regain of jute, but is not capable of great accuracy because a relatively small difference in density may correspond to a large difference in regain.

### Swelling

The equation relating swelling and specific gravity can be obtained from the following considerations

Let  $\Delta_t$  = true specific gravity of dry fibre

$\Delta_a$  = apparent specific gravity of dry fibre

$R$  = absorption in grams of water by 100 grams of dry fibre

$S$  = swelling in c.c. per c.c. of fibre

Since dry fibre weighing 1 gm. and having volume of  $\frac{1}{\Delta_t}$  c.c. absorbs on immersion in water  $\frac{R}{100}$  c.c. of water and swells by  $\frac{S}{\Delta_t}$  c.c. the apparent specific volume—

$$\frac{1}{\Delta_a} = \frac{1}{\Delta_t} + \frac{S}{\Delta_t} - \frac{R}{100} \dots \dots \dots 2$$

When the apparent and true specific gravities, as well as the regain, are known, swelling can be calculated by substituting in equation 2. If  $\frac{S}{\Delta_t} = \frac{R}{100}$ , then  $\frac{I}{\Delta_a} = \frac{I}{\Delta_t}$ , i.e., true and apparent specific gravities are equal. In the case of fibre  $\frac{S}{\Delta_t}$  is always less than  $\frac{R}{100}$  since the volume of liquid absorbed by the fibre is greater than the amount by which it swells, and the ratio  $\frac{R}{100} : \frac{S}{\Delta_t}$ , i.e. volume of liquid required to produce a swelling of 1 c.c. is called the compression factor, the liquid on entering the fibres apparently occupying a smaller volume. This may be attributed to (a) the filling up of cavities within the fibre without increase in external dimensions, or (b) real compression caused by swelling of contiguous structural units of fibre.

## EXPERIMENTAL

### Dry Weight

For the determination of true specific gravity the fibre must be absolutely dry, and in the present investigation the methods employed by Urquhart and Williams<sup>10</sup> for cotton, and Barritt and King<sup>11</sup> for wool were adopted. The former method depends on the use of phosphorus pentoxide in a vacuum desiccator under reduced pressure, and the latter on heating to constant weight in a specially constructed regain bottle at a temperature of 110° C in a continuous current of dry air. The effects of different temperatures, and of using air of 65-70 per cent relative humidity, were examined by means of the regain bottle.

*Preparation of the Fibre.*—Prior to the actual estimations the fibres were cleaned and prepared by washing successively in a 0.1 per cent neutral soap solution, alcohol and ether, air-drying, and then exposing to an atmosphere maintained at 65-70 per cent relative humidity (70° F.) for a minimum period of 48 hours.

*Desiccator Method.*—Ten numbered weighing bottles of 25 mm. diameter were weighed empty and after the introduction of the fibre they were placed, with the stoppers removed, in a vacuum desiccator under reduced pressure over phosphorus pentoxide. At 48 hour intervals the pressure was allowed to rise by admitting air through a calcium chloride tube, the desiccator opened, the stoppers instantly replaced, and the bottles weighed until constant weights were obtained for three consecutive weighings of each bottle. The minimum time to reach constant weight was 14 days. The results obtained were checked by re-conditioning and again determining the dry weight. The duplicate results agreed in every case and were accepted as the bone-dry weights of the samples under examination.

*Regain Bottle Method.*—The dry fibre from one of the sample bottles was transferred to a weighed regain bottle and two series of experiments were conducted. In one the inlet of the bottle was open to the conditioned atmosphere, and the outlet was connected to a calcium chloride tube, joined



to an exhaust pump so that conditioned air of known humidity could be drawn through the regain bottle. In the second series of experiments the inlet of the bottle was connected with a calcium chloride tube, which in turn was joined to a wash-bottle containing strong sulphuric acid. The outlet was connected with another calcium chloride tube, to which the exhaust pump was joined. In this manner dry air was drawn through the regain bottle, which was heated to different temperatures in a specially constructed electric oven. The heating and the suction of air were continued for 2 hours when the pump was stopped, and the heater was cut off, and the regain bottle with its contents allowed to remain connected with the drying tube for 30 minutes to enable it to cool to room temperature, before being weighed. The procedure was repeated for a second period of one hour to ensure that constant weight had been obtained. For the determination of true specific gravity the fibre samples were all dried to constant weight in a current of dry air, at a temperature of  $110^{\circ}\text{C}.$ , in the regain bottle.

### Specific Gravity

The dry fibre, prepared and weighed as described, was rapidly introduced into a 50 cc. specific gravity bottle of known weight. The bottle was fitted with a T-piece, having a 3-way cock, and one terminal of the T-piece was connected to an exhaust pump (Cenco Hyvac), while the other was coupled to the flask containing the liquid used in the determination. The bottle was evacuated for 30 minutes and connected to the flask containing the appropriate liquid, which was allowed to fill the bottle completely. The bottle containing the fibre and liquid was weighed after standing for half-an-hour at room temperature. From the dry weight of fibre, the weight of fibre and the liquid, the weight of the liquid and that of water completely filling the bottle, it was possible to find the true specific gravity of the fibre. The experiments were all conducted in a conditioned atmosphere to ensure temperature control throughout, and weighings were carried out on a balance of high sensitivity.

The object of using the exhaust pump to de-aerate the fibre was to ensure complete wetting. The medium used to determine the true specific gravity of the fibre should not cause swelling and should have high wetting power and low surface tension so that air entrapped between the fibres may be easily removed. The liquids used were water, benzene, carbon-tetrachloride, acetone and mineral oil, and of these benzene and mineral oil have been previously shown not to cause swelling. The solvents were all of Merck's extra pure quality, and were completely de-hydrated over calcium chloride and tested with anhydrous copper sulphate prior to use.

The effect of incomplete wetting was shown by measuring the specific gravity at different time intervals of de-aeration. Benzene, carbon-tetrachloride and acetone have low surface tensions and the specific gravities found by using these solvents showed little variation as the result of evacuation, and, consequently, wetting was complete without the necessity of this operation. Mineral oil showed an increase in specific gravity as the result of evacuation, and water an appreciably greater increase, indicating that the removal of air-bubbles is necessary if accurate determinations are to be obtained. The results are shown in Table I.

Table I

Liquid used	Specific Gravity		
	Without evacuation	Evacuation for $\frac{1}{2}$ hour	Evacuation for 1 hour
Water	1.367	1.557	1.564
Benzene	1.445	1.455	1.461
Carbon-Tetrachloride	1.426	1.436	1.431
Acetone	1.558	1.548	1.560
Mineral oil	1.389	1.440	1.438

### Swelling

Burdick<sup>12</sup> has shown that the change in elongation of jute fibre at constant tension, due to increase in atmospheric humidity from 20 per cent to 95 per cent is approximately 0.14 per cent and consequently the swelling of jute fibre in the longitudinal direction can be regarded as negligible in comparison with the lateral swelling. The volume swelling, as calculated from specific gravity measurements should, therefore, agree with the swelling determined by observations on cross sections. Observations were made on cross sections of fibres by means of a projection microscope. A bunch of prepared fibres, suitably dried, was instantly immersed in xylene to prevent any error due to contact with air and consequent swelling. Benzene was not used on account of its relatively high rate of evaporation. Cross sections of these fibres were cut, using Wollhaf's<sup>13</sup> method. The fibres were kept saturated with xylene and, after the section was cut, a final drop of xylene was added prior to fixing the cover glass. The slide was mounted on a vertical projection microscope, provided with an objective and eye-piece of magnification  $25\times$  and  $4\times$  respectively. The source of illumination was a 12 volt 2 ampere lamp, fitted at the apex of the instrument, and the magnification of the image focussed on a white polished circular disc at the base was 500. The outlines of the sections were traced on white paper placed over the disc. The cover glass was then removed, the xylene was allowed to evaporate, and the fibre cross section was saturated with a drop of distilled water before the cover glass was replaced. Special precautions were taken to ensure that the slide was not moved, in order to maintain the same sections in their identical positions in the field. Outlines of the swollen sections were drawn on the same paper by means of a coloured pencil, in order to distinguish from the unswollen sections. The areas of sections were measured by means of a compensating planimeter, so that the actual cross sectional areas of the fibres could be evaluated on dividing by  $500^2$  (square of the magnification). The area of each section was thus measured before and after swelling and the percentage swelling calculated. Five sets of measurements in five different fields, each of 100 sections, were taken, and the mean swelling was calculated from the total of 500 measurements.

### Diameter Swelling Measurements

Measurements of diameter swelling were made by means of an ordinary microscope to examine whether any relation existed between diameter and swelling. 20 fibres were fixed on a glass slide with a solution of asphalt in chloroform and 50 measurements recorded for each fibre at intervals of 0.1

mm 1,000 measurements were recorded in this manner in air and again in distilled water (pH 7) Since the observations continued over a prolonged period of about 12 hours, the dry diameter was taken in air instead of in glycerine, benzene, or any other non-swelling medium, which have either a tendency to absorb moisture or to evaporate rapidly Although the humidity and temperature of the air, during the period over which the diameters were measured, were not constant the variation was not considered sufficient to affect the result and the large number of readings taken served further to reduce any error due to this cause Individual readings in air were divided into groups Readings of 9 to 10 micrometer divisions were grouped and their average found. Similarly for micrometer readings 11 to 12, 13 to 14, etc. The same procedure was used for the corresponding readings in water for each group, and the difference between the respective averages in air and those in water expressed as a percentage of the average in air, gives the swelling.

## RESULTS

### Dry Weight of Jute

Regain bottle measurements on a sample of fibre, previously dried by the desiccator method, and in a current of conditioned air (65 per cent relative humidity) and dry air at different temperatures, are shown in Tables II and III.

**Table II**  
Weight of jute heated to different temperatures in a current of conditioned air (relative humidity 65% at 70° F. at intake)

Temperature °C	Weight (gms )	Weight expressed on desiccator dry weight (0.9938 $\equiv$ 100)
20	1.0990	110.6
40	1.0424	104.9
60	1.0220	102.8
80	1.0070	101.3
110	0.9988	100.5
20	1.0972	110.4

**Table III**  
Weight of jute heated to different temperatures in a current of dry air.

Temperature °C.	Weight (gms )	Weight expressed on desiccator dry weight ((0.9938 $\equiv$ 100)
20	1.0166	102.2
40	1.0056	101.2
60	0.9998	100.6
80	0.9964	100.3
110	0.9932	99.9
20	1.0962	110.3
(Conditioned air passed through)		
20	1.0142	102.1
(Dry air passed through)		
110	0.9922	99.8
140	0.9898	99.6

Examination of Table II shows that jute heated to  $110^{\circ}\text{C}$ ., in a current of air (65 per cent Relative Humidity at  $70^{\circ}\text{F}$  at intake), retains 0.5 per cent moisture when compared with the dry weight over phosphorus pentoxide expressed as 100. This condition is normally obtained in a conditioning oven, where air with an initial moisture content at a lower room temperature is simply heated to  $110^{\circ}\text{C}$ ., and should thus still contain moisture—the quantity of which is dependent on the initial relative humidity of the air itself. Provided other limitations and sources of error in a conditioning oven, as indicated by Stephenson<sup>11</sup>, are neglected for purposes of comparison, the dry weight as determined with a commercial conditioning

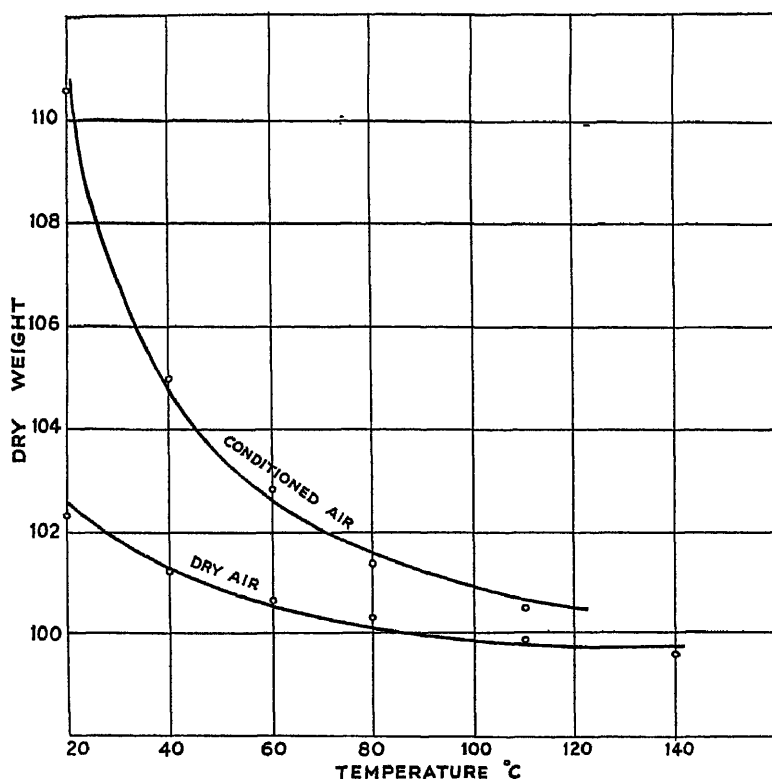


FIG. 1.

oven should, therefore, be at least 0.5 per cent higher than the true or absolute dry weight and regain determination would, accordingly, be correspondingly lower. From Tables II and III it is evident that jute fibres re-conditioned to an atmosphere of 65 per cent. relative humidity and  $20^{\circ}\text{C}$ .—after having been heated to  $110^{\circ}\text{C}$ —show a diminished weight. That this diminished weight is not due to loss of constituents other than moisture was concluded from an experiment with three weighing bottles containing jute fibres, the dried weights of which had been determined over phosphorus pentoxide. The bottles were heated in a thermostatically controlled laboratory conditioning oven at  $110^{\circ}\text{C}$  for 6 hours, removed, and the dry weights again determined. The results showed no change in the dry

weights as an outcome of heating and, consequently, decrease of conditioned weight after heating must be due to the moisture-absorbing capacity of the jute being reduced. Table III indicates that the dry weight of jute fibres, heated at  $110^{\circ}\text{C}$  in a current of air is 99 g compared with the desiccator dry weight of 100. The regain bottle method, it would thus appear, is not only more rapid but also equally accurate. At  $170^{\circ}\text{C}$  the weight was found to decrease very rapidly and the fibres are charred to a dark brown colour. The highest limit to which jute fibres can be heated without charring and decomposition must lie between  $140^{\circ}\text{C}$  and  $170^{\circ}\text{C}$ , but no effort was made to find this maximum temperature since the additional loss in weight at temperatures above  $110^{\circ}\text{C}$ , is so small that, for commercial purposes, it can be disregarded. This is clearly shown from the curves in the graphs in Fig 1, which illustrate the comparative effect of drying in dry and conditioned air, the temperature remaining the same in each case.

#### Specific Gravity.

Three measurements were made with each liquid used, and the mean taken as the specific gravity for the corresponding liquid. The results are given in Table IV.

Table IV

Liquid used	Serial No of experiment	Dry weight of jute	Weight of liquid displaced	Sp gr of liquid relative to Water at $70^{\circ}\text{F}$	Sp gr of jute relative to Water at $70^{\circ}\text{F}$ .	Mean sp. gr. of jute relative to Water at $70^{\circ}\text{F}$
Water	1	2.1242	1.3596	1	1.562	1.559
	2	2.1836	1.3996	1	1.559	
	3	2.8214	1.8124	1	1.557	
Benzene	1	3.2238	1.9578	0.8794	1.448	1.463
	2	1.8894	1.1184	0.8794	1.486	
	3	2.1288	1.2868	0.8794	1.455	
Carbon Tetrachloride	1	2.2212	2.4486	1.595	1.446	1.436
	2	2.2588	2.5028	1.595	1.440	
	3	1.5612	1.7502	1.595	1.423	
Acetone	1	1.8816	0.9456	0.7938	1.580	1.568
	2	1.8044	0.9024	0.7938	1.586	
	3	2.7158	1.4018	0.7938	1.536	
Mineral oil	1	3.5060	2.2108	0.9177	1.455	1.440
	2	3.4298	2.2038	0.9177	1.428	
	3	1.9822	1.2644	0.9177	1.438	

The high values found with water and acetone are probably due to absorption of the liquids by the fibres with consequent swelling. Carbon-tetrachloride and mineral oil give practically identical values, but benzene is slightly higher. This may be due to traces of moisture in the liquid, although precautions were taken, or to slight absorption. In consequence the regain of dry fibres towards the vapour of the liquids used was next

examined in a similar manner to the regain for water vapour. Five samples of fibres, in separate weighing bottles, were dried to constant weight over phosphorus pentoxide and each bottle was hung inside an air-tight container over the appropriate liquid. A weighing bottle containing calcium chloride was placed in each container—except the one with water inside. The bottles with the jute samples were removed after a week, quickly stoppered, re-weighed, and the corresponding regain found from the difference in weights. The results are shown in Table V.

Table V

Liquid used	Weight of weighing bottle (empty)	Weight of weighing bottle + jute after drying over phosphorus pentoxide	Dry weight of jute	Weight of weighing bottle + jute after 1 week in vapour above liquid	Weight of jute after 1 week in vapour above liquid	Regain %
Water	18 7808	19 9316	1 1508	20 2984	1 5176	32
Benzene	20 2988	21 3000	1 0012	21 3288	1 0300	3
Carbon Tetrachloride	21 2944	22 3040	1 0096	22 3368	1 0424	3
Acetone	20 1320	21 0986	0 9666	21 2944	1 1624	20
Mineral oil	20 1732	21 1618	0 9886	21 2009	1 0277	4

The behaviour of acetone and water is shown to be similar, the regain being high in both cases. Benzene, carbon-tetrachloride and mineral oil, on the other hand, are characterised by very small regains of 3 to 4 per cent. Since mineral oil has a negligible vapour pressure it is unlikely that the saturation regain would be reached in one week and, consequently, the regain figures found of 3 to 4 per cent. are most probably due to traces of residual atmospheric moisture. Table IV indicates that the true specific gravities in carbon-tetrachloride and mineral oil are, to all intents and purposes, the same. A slightly higher value has been found for benzene, which may thus be due to a trace of moisture present in the benzene itself. The true specific gravity of jute fibres is, therefore, given as 1.436 and the apparent specific gravity (i.e. the specific gravity in water) is 1.559.

The apparent specific gravity of fibres of known regain can be calculated from equation 1. If Pfuhl's value of 37 per cent regain for jute conditioned at 100 per cent R.H. is accepted, the apparent specific gravity

$$\Delta_a = \frac{100 + 37}{1.559} = 1.356$$

The actual measurement of apparent specific gravity on 6 different samples of jute conditioned at 100 per cent. R.H. (70° F) are shown in Table VI. The fibres were suspended over water in a desiccator for one week.

Table VI

No of sample	Weight of jute	Weight of water displaced	Sp gr. of jute relative to Water at 70° F	Mean sp. gr. relative to Water at 70° F
1	1.2472	0.9258	1.347	1.359
2	0.9696	0.7148	1.357	
3	2.4334	1.7986	1.353	
4	1.8344	1.3452	1.364	
5	1.7834	1.3036	1.368	
6	1.1968	0.8788	1.362	

The mean value is in excellent agreement with the calculated value of 1.356. Equation 1 may also be used to calculate regain if  $\Delta_a$  at the corresponding regain is known.

#### Swelling

The volume swelling (S) of jute fibres is found from equation 2 by substituting  $\Delta_t = 1.436$  and  $\Delta_a = 1.559$  and  $R = 37$  per cent. (Pfuhl's value).

$$\frac{1}{1.559} = \frac{1}{1.436} + \frac{S}{1.436} - \frac{37}{100}$$

$$\therefore S = 0.45$$

$$= 45\% \text{ by volume.}$$

The compression factor  $\frac{R}{100} \frac{S}{\Delta_t}$ , i.e. the volume of water required to produce a swelling of 1 cc

$$= \frac{37}{100} \frac{0.45}{1.436}$$

$$= 1.19$$

Thus, 100 cc of fibres when immersed in water swell by 45 cc and absorb  $1.19 \times 45 = 54$  cc of water. This apparent compression of 9 cc may be attributed to one or both of the causes, namely, filling up of cavities, and compression due to swelling

Since jute fibres are composed of irregular polygonal cells, each with a central cavity or lumen, whose average area—expressed as a percentage of the average cross-sectional area—is also of the same order of magnitude it seems to indicate that the apparent compression is mainly due to the filling up of these lumens, and actual compression, if such does occur, is very small.

#### Swelling of Cross-Sections

It has been previously indicated that volume swelling of fibres calculated from specific gravities should agree with the value found experimentally from measurements of cross-sections. The results of experiment on only

one sample of fibres are given in Table VII, where the areas of cross-sections in xylene and water are included with the probable error of each measurement. Five sets of 100 measurements were taken.

Table VII  
Area of Cross-Sections of Fibres (Mean of 100 Observations)

No.	Area of cross section in xylene $\times 10^6$ sq cms	Probable error $\times 10^6$	Area of cross section in water $\times 10^6$ sq cms	Probable error $\times 10^6$	Swelling %	Mean Swelling %
1	11.6	0.32	15.6	0.38	32	40
2	10.0	0.30	14.0	0.35	40	
3	16.8	0.22	10.0	0.30	47	
4	18.0	0.24	11.4	0.32	43	
5	10.6	0.08	14.6	0.35	38	

Swelling is shown to decrease with increase of area from 47 per cent. to 34 per cent. The mean swelling is 40 per cent, which is in fair agreement with the calculated value of 45 per cent—taking into consideration the relatively low order of accuracy of the cross-section area method.

A summary of diameter swelling measurements, using an ordinary microscope, is given in Table VIII.

Table VIII

Average diameter in air	Average diameter in water	Swelling %
9.5	17.3	82.1
11.6	18.0	55.2
13.6	19.1	40.4
15.5	19.7	27.1
17.5	21.9	25.1
19.4	23.1	19.1
21.4	23.7	10.7
23.5	26.0	10.6
25.3	27.6	9.1
27.4	30.0	9.5

The results indicate that swelling diminishes with increase of diameter, as concluded from measurements with the projection microscope, and the decrease is at first rapid and then slow. A similar relation between diameter and swelling has been found for cotton by Kusebach<sup>15</sup> and for silk fibroin by Ingram<sup>16</sup>.

#### SUMMARY

The true and apparent specific gravities of dry jute fibres have been found to be 1.436 and 1.559 respectively.

The volume swelling of fibres calculated from the specific gravity is 45 per cent.

Measurements on cross-sections as well as on diameters indicate that swelling diminishes with increase of area or diameter of fibres.

The effect of temperature and humidity on dry weights of fibres has been investigated.



Thanks are due to the Indian Jute Mills Association for permission to publish this paper and to Dr S G Barker for his helpful comments in reading the original proof.

Indian Jute Mills Association,  
Research Laboratories, Calcutta  
*September 28th, 1940*

#### REFERENCES

- <sup>1</sup> W G Macmillan & M K Sen *J Text Inst*, 1939, 30, 173
- <sup>2</sup> A. T King *J Text Inst*, 1926, 17, 153
- <sup>3</sup> F. T. Peirce *J. Text Inst*, 1923, 14, 11
- <sup>4</sup> G G Clegg, *J Text Inst*, 1924, 15, 11
- <sup>5</sup> J A. Matthew *J Text, Inst* 1921, 12, 1469
- <sup>6</sup> M H Preston and J A Matthew *J Text Inst*, 1934, 25, 1311
- <sup>7</sup> L Vignon *Compt Rend*, 1892, 114, 424
- <sup>8</sup> J Kubota *Bull Ser Silk Ind.*, 1932, 5, 9
- <sup>9</sup> A C Goodings and L H Turl *J Text Inst*, 1940, 31, 169
- <sup>10</sup> A R Urquhart and A M Williams *J Text Inst*, 1924, 15, 1138
- <sup>11</sup> J Barritt and A T King *J Text Inst*, 1926, 17, 1386.
- <sup>12</sup> C L Burdick Private communication
- <sup>13</sup> A Wollhaf *Die Kunstseide*, 1930, 12, 422.
- <sup>14</sup> H. Stephenson *J Text Inst*, 1938, 29, 1297.
- <sup>15</sup> K Kusebach *Mell Textber*, 1934, 15, 193.
- <sup>16</sup> R V Ingram. *Text. Res*, 1938, 9, 79

*Received 29/11/40*

# THE JOURNAL OF THE TEXTILE INSTITUTE

## TRANSACTIONS

### 6—A COMPARISON OF THE RATES OF FLOW OF MODIFIED COTTON CELLULOSES DISSOLVED IN SOLUTIONS OF TRIMETHYLBENZYLAMMONIUM HYDROXIDE (TRITON B), DIMETHYLDIBENZYLAMMONIUM HYDROXIDE (TRITON F), SODIUM HYDROXIDE, CUPRAMMONIUM AND CUPRI-ETHYLENEDIAMINE.

By T. BROWSETT and D. A. CLIBBENS

(The British Cotton Industry Research Association)

(Copyright by the Textile Institute)

The rate of flow of cellulose solutions has acquired importance, first, as a means for describing, specifying and testing important technical qualities of cellulose materials. For this purpose the only cellulose solvent that has so far proved of general utility is cuprammonium hydroxide, which is in some respects far from ideal. The good solvent action of dimethyldibenzylammonium hydroxide,<sup>1</sup> and its appearance on the market as Triton F (Rohm & Haas Co.), suggest that it might be a useful alternative dispersing agent in rate of flow measurements made for specification or testing purposes. The other bases with which this paper is concerned are not sufficiently good cellulose solvents to be of general utility with the exception of cupri-ethylenediamine, which offers little advantage over cuprammonium to compensate for some serious disadvantages. A useful scale of cellulose quality is obtained by expressing rate of flow measurements made on 0.5 per cent. cellulose solutions in absolute fluidity units, and comparisons are therefore made in this paper between the absolute fluidities at 20° C. of 0.5 per cent solutions of cotton cellulose chemically modified in several different ways, when dispersed in cuprammonium and in Triton F.

Secondly, the rate of flow of cellulose solutions has acquired importance as a method for investigating fundamental properties of the dissolved cellulose, such as its mean molecular weight. For this purpose, the rate of flow must be expressed as a relative viscosity ( $\eta_r$ ) or as the increase in relative viscosity of the liquid caused by the dissolution of the cellulose—called the specific viscosity of the solution ( $\eta_{sp} = \eta_r - 1$ ). Comparisons are therefore made between the specific viscosities at 20° C. of 0.5 per cent modified cotton dispersions in cuprammonium, dimethyldibenzylammonium hydroxide (Triton F), trimethylbenzylammonium hydroxide (Triton B), sodium hydroxide and cupri-ethylenediamine.

The expression of the rate of flow of cellulose solutions in viscosity units for the description of cellulose quality has the disadvantage that a series of modified products judged to be spaced in a roughly uniform way by many chemical and physical properties of direct practical importance are very unevenly distributed over the viscosity scale. The two different forms in which the results will be presented thus reflect the two slightly different aspects from which the comparisons are made.

**The Fluidity of Modified Cottons in Triton F and in Cuprammonium**

The fluidity of the cuprammonium solvent is about 72 c.g.s. units at 20° C. For measurements made in Triton F, a solution 2.0*N* in titratable base was chosen as solvent, and at this concentration—which is near the maximum in the solubility curve<sup>1</sup>—the fluidity of the sample of Triton F employed was about 14 c.g.s. units at 20° C. The solvent is thus much less fluid than cuprammonium, so that one of the results of changing from cuprammonium to Triton F is to shift all measurements on 0.5 per cent. cellulose dispersions to a lower range of absolute fluidity. The viscometric method used was similar to that developed in these laboratories for cuprammonium solutions of cellulose.<sup>2</sup>

The starting material for all the modified cottons examined was a carefully bleached cotton linters of fluidity 5.6 in cuprammonium. This was progressively modified by different controlled chemical treatments in such a way as to produce several series of modified cottons covering a range of fluidity in cuprammonium up to about 40. One such series was prepared by each of the following chemical treatments, all at the ordinary temperature: (i) Hydrolysis with aqueous hydrochloric acid, (ii) Oxidation with dichromate in dilute sulphuric acid solution, (iii) Oxidation with hypochlorite solution buffered near pH 7, (iv) Oxidation with dichromate solution in the presence of oxalic acid, (v) Oxidation with dilute periodic acid solution, and (vi) Oxidation with hypobromite in dilute sodium hydroxide solution. Fig. 1 shows the relation between the absolute fluidities in the two solvents for the first three of these series, the curves being numbered as above. The remaining three series of oxycelluloses yield curves almost coinciding with No. 1 for hydrocelluloses, but slightly displaced from it in the same direction as the other oxycelluloses, results for them have not been included in the figure for the sake of graphical clarity. It is seen that no unique relation applicable to the whole family of chemically modified cottons exists between the fluidities of 0.5 per cent. dispersions in the two solvents.

From each of the six series of materials chemically modified in different ways as already listed, and including those represented by Curves 1, 2 and 3 of Fig. 1, two were selected of fluidities about 3 and 5 in Triton F. They were all treated with 0.1*N* sodium hydroxide for 24 hours at the room temperature, washed, and their fluidities again measured in both solvents. The results for the treated materials are represented by the two groups of six points not enclosed by triangles, etc., lying close to Curve 1 in Fig. 1, and they show that the effect of the treatment is to close up the curves until they all nearly coincide with that for the untreated hydrocelluloses. The precise effect of the alkaline treatment on the two oxycelluloses in the neutral hypochlorite, and in the dichromate/sulphuric acid, series is shown in the figure by lines connecting the points that represent their properties before and after the treatment. It is seen to consist of a rise in cuprammonium fluidity unaccompanied by any considerable change in Triton fluidity. With the hydrocelluloses, the alkaline treatment produces little change of fluidity in either solvent. Of the oxycellulose series not depicted in Fig. 1 because they yield curves close to No. 1, the products of hypobromite, and of dichromate/oxalic acid, oxidation show small rises in fluidity in both solvents as a result of the alkaline treatment, whilst the products of periodic acid oxidation show small falls in both solvents. The points representing them thus suffer a slight displacement, which moves them up or down the

original curve, but not away from it. Almost identically the same results are produced by boiling the materials with 0.25*N* sodium hydroxide solution.

The experimental observations are to be explained in terms of the action of different alkalis on oxycelluloses formed in neutral or acid oxidising media, which exhibit the property called alkali-sensitivity. This subject has been studied by Davidson<sup>3</sup>, and the conclusions outlined below were established by a study of the fluidity of nitrocelluloses derived from modified cottons, having been suggested in part by studies of the effect of chemical modification on the tensile strength of cotton. When cotton is oxidised in neutral or acid solution the products formed contain some chain-molecules that are only fragments of the originals, and among, or in addition to, them some that have been rendered peculiarly sensitive to alkalis so that a further fragmentation of chain-molecules is brought about when the oxidised

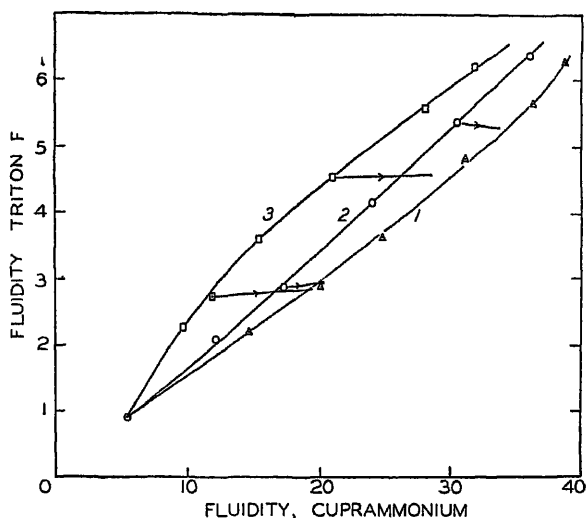


Fig. 1  
Relation of fluidity in cuprammonium to that in Triton F

- (1) Hydrocelluloses
- (2) Dichromate/sulphuric acid oxycelluloses
- (3) Neutral hypochlorite oxycelluloses

Unenclosed points various oxycelluloses and hydrocelluloses after treatment with 0.1*N* sodium hydroxide

materials are submitted even to very mild alkaline treatments. This additional fragmentation is effected both by the alkaline action of cold dilute sodium hydroxide, which is not a cellulose solvent, and by that of cuprammonium hydroxide, which dissolves the cellulose, but the extent of the effect may differ greatly with the two alkalis. The difference in their action is not observed, or not in the same degree, with all alkali-sensitive oxycelluloses, but it is particularly characteristic of the products formed by the oxidation of cotton in neutral or acid hypochlorite solution, in which cold dilute sodium hydroxide produces greater additional degradation than the cuprammonium solvent. It is for this reason that treatment with dilute sodium hydroxide causes a considerable rise in the cuprammonium fluidity of such oxycelluloses.

The simplest conditions for comparing the flow properties of a modified cellulose in two different alkaline solvents, such as cuprammonium and

Triton F, are naturally those in which neither solvent alters the chain-length distribution. These conditions are assured only with the hydrocelluloses, for which the relation between fluidities in the two solvents is given by Curve 1 in Fig. 1. They are approximately met by oxycelluloses formed in alkaline media, and the products of oxidation with alkaline hypobromite yield a curve approximating to that for hydrocelluloses in Fig. 1. If the chain-length distribution of the modified cellulose is altered by the action of alkalis, the conditions will yet remain simple if the two alkaline solvents compared exert the same effect. These are the conditions postulated for the highly alkali-sensitive products of oxidation with periodic acid, and with dichromate/oxalic acid, which also yield curves lying close to that for the hydrocelluloses. But if the two alkaline solvents compared exert different effects on an alkali-sensitive oxycellulose, the conditions are complicated by the fact that the fluidities in different solvents are functions of different chain-length distributions. These conditions are postulated for the products of oxidation with dichromate/sulphuric acid and with neutral hypochlorite in order to explain why the relation between their fluidities in the two solvents differs widely from that shown by other modified celluloses. This explanation is strongly supported by comparing the effects of the standard non-solvent alkaline treatment of the materials with sodium hydroxide on their fluidities in the two alkaline solvents. It has been seen that for all the modified cottons that yield curves near to No. 1 in Fig. 1, treatment with 0.1*N* sodium hydroxide for 24 hours at 18° C. either has no appreciable effect on fluidity in either solvent, or alters it in a similar way in both. For the modified cottons represented by Curves 2 and 3, however, the same treatment causes a large increase of cuprammonium fluidity unaccompanied by any significant change in Triton fluidity. Sodium hydroxide thus produces a greater effect than cuprammonium but not greater than that of Triton F. It is to be concluded that although these oxycelluloses suffer some reduction in average chain-length under the influence of both solvents, they are less affected in this sense by cuprammonium than by Triton F. Hence the cuprammonium fluidity of an oxycellulose of given Triton fluidity must appear abnormally low judged by the relation obtained for modified cottons that do not reflect specific differences between the actions of different alkalis.

While this paper was in preparation, comparisons were published by Russell and Woodberry<sup>4</sup> of fluidity measurements in Triton F and cuprammonium made on bleached cotton materials before and after numerous commercial launderings. These materials formed a series of chemically modified products covering a range of cuprammonium fluidity up to about 30 in 0.5 per cent dispersions, but their exact chemical history is unspecified. For the study of 0.5 per cent cellulose dispersions in Triton F, a solution 1.96*N* in titratable base was used by these authors, no special precautions were employed by them to avoid access of air in the preparation of the cellulose dispersions, and the measurement of fluidity was made at 25° C in a U-tube type of viscometer. The authors conclude that the relation between the fluidities in the two solvents is approximately a linear one over a range of cuprammonium fluidity from 4 to 25, and is such that the absolute fluidity of the cuprammonium dispersion is ten times that of the Triton dispersion. It seems probable that the chemical degradation of the cottons used for this comparison was a result of oxidative attack in an alkaline medium, since it was produced in laundry operations. In this case,

the materials would not be appreciably alkali-sensitive and the results of Russell and Woodberry should be comparable with those represented by Curve 1 in Fig. 1. Up to a cuprammonium fluidity of 25, this curve does not diverge appreciably from a linear course, for which, however, the cuprammonium fluidity is about seven times the Triton fluidity, instead of ten times as found by Russell and Woodberry. The comparisons of rate of flow in this paper were made at 20° C, those of Russell and Woodberry at 25° C, but this seems insufficient to account for the apparent discrepancy, the cause of which is not clear.

A consideration of the relative advantages of Triton F and cuprammonium as solvents for specifying and controlling the flow properties of cellulose dispersions leads to the following conclusions. The abnormal action of cuprammonium on some alkali-sensitive oxycelluloses when compared with the action of non-solvent alkalis, and the normal action of Triton F, endow the latter with a definite advantage. In order to assess the total chemical deterioration, actual and potential, in a sample of cellulose of unknown chemical history the material should be treated with sodium hydroxide before measurement of its fluidity in cuprammonium, but this pre-treatment is not necessary for fluidity measurements made in Triton F. The greater stability of the organic base is a further advantage of this solvent. The work of Russell and Woodberry suggests that the oxidation of cellulose by air may be so much slower in Triton than in cuprammonium dispersions that a technique involving exclusion of air might for some purposes be unnecessary, but there is at present insufficient evidence on this point.

The lower fluidity range in which the Triton measurements must be made is a slight disadvantage, but of more concern is the uncertainty whether or not the base can be produced commercially of a sufficiently standard quality in respect to its solvent power for cellulose, and the fluidity of cellulose-dispersions in it. The total titratable base in the commercial solution does not at present provide adequate quality control in these respects.<sup>1</sup>

#### **The Specific Viscosities of Modified Cottons in five different basic Solvents**

Simple recalculation of data already depicted enables a comparison to be made between the specific viscosities of 0.5 per cent. cellulose dispersions in cuprammonium and dimethyldibenzylammonium hydroxide (Triton F) at 20° C. Fig. 2 shows the relation between the two for hydro-celluloses (Curve 1), oxycelluloses formed with dichromate in sulphuric acid solution (Curve 2), and oxycelluloses formed with neutral hypochlorite solution (Curve 3). These curves depict the same experimental data as the corresponding curves of Fig. 1 in the plot of absolute fluidities, and the unenclosed points lying near Curve 1 again represent pairs of all the six types of modified cotton studied, after the materials had been treated with cold dilute sodium hydroxide. The straight line OP is that corresponding to equal specific viscosities in the two solvents. The figure shows that hydro-celluloses, for which the chain-length distribution is the same in the two solvents, have a higher specific viscosity in Triton F than in cuprammonium. In the range of lower viscosities the corresponding curve No. 1 approximates to a straight line for which the specific viscosity in Triton F is 1.55 times that in cuprammonium. The effect of the alkali-sensitivity of certain oxycelluloses in altering this relation has already been described, and is so pronounced in the hypochlorite oxycelluloses that for some of them the

specific viscosity in Triton F is lower than in cuprammonium. The corresponding curve No. 3 in Fig. 2 is not a straight line, and for these oxycelluloses the ratio of the specific viscosity in Triton F to that in cuprammonium varies from about 0.8 to 1.05 with increasing degradation. The dichromate/sulphuric acid oxycelluloses are intermediate, and for them the ratio is about 1.25. All three curves converge to a point representing the bleached cotton linters from which the different series of modified materials were prepared, but this point lies far off the figure to the right, and could not be included without greatly enlarging it or inconveniently reducing the scales.

For measurements of the rate of flow of 0.5 per cent. dispersions in cupri-ethylenediamine at 20° C., the solvent was prepared by saturating 0.4*M* ethylenediamine with copper hydroxide. It is inherently unstable, and slow auto-reduction of cupric to cuprous copper occurs. The fluidity of the solvent

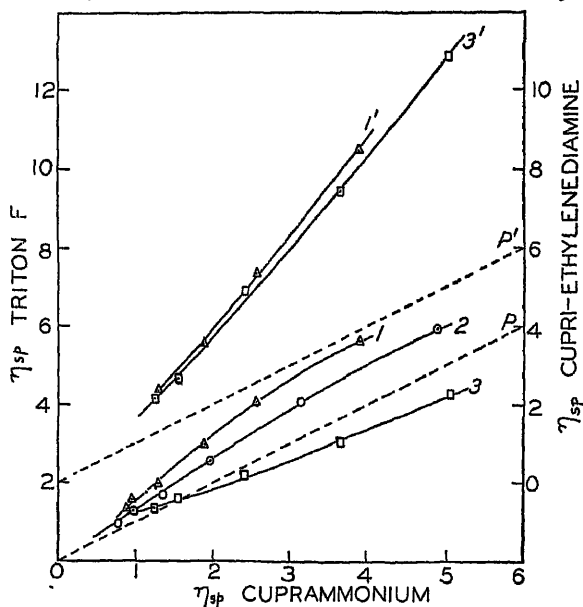


Fig. 2 Relation of specific viscosity in cuprammonium to that in Triton (1, 2, 3) and in cupri-ethylenediamine (1', 3')

- 1, 1' Hydrocelluloses
- 2 Dichromate/sulphuric acid oxycelluloses
- 3, 3' Neutral hypochlorite oxycelluloses.

was about 88.5 c.g.s. units, and the method used was the same as that for cuprammonium solutions in cellulose. Curves 1' and 3' in Fig. 2 show the relations between the specific viscosities in the two cupric-ammine bases for the hydrocelluloses and the oxycelluloses formed by oxidation with neutral hypochlorite solution, they correspond to the Curves 1 and 3 in the comparison between the quaternary ammonium base and cuprammonium. The two vertical scales in Fig. 2, measuring specific viscosities in Triton F and cupri-ethylenediamine, have been shifted relatively to one another in order to separate the curves, and the line 2P' is the one representing equal specific viscosities in cupri-ethylenediamine and cuprammonium. The relation between the specific viscosities in the two complex bases is very nearly the same for the two different kinds of modified cottons. The specific viscosity in cupri-ethylenediamine is much greater than that in cuprammonium, the ratio varying from about 2.2 to 1.7 with increasing degradation. The close

approach of Curves 1' and 3' shows that cupri-ethylenediamine and cuprammonium alter the chain-length distribution of the alkali-sensitive hypochlorite oxycelluloses in a similar way, and hence both actions differ from that of dilute sodium hydroxide. The fluidity or viscosity of a neutral hypochlorite oxycellulose in cupri-ethylenediamine solution is in fact greatly altered by treatment of the material with dilute sodium hydroxide, the effect being similar to that exerted on the flow properties in cuprammonium solution. In a plot of Triton F against cupri-ethylenediamine viscosities, the curve for hydrocelluloses would obviously diverge widely from that for the neutral hypochlorite oxycelluloses, just as do the curves 1 and 3, which show the relation between Triton F and cuprammonium viscosities.

Some measurements of the rate of flow at 20° C. have also been made for 0.5 per cent dispersions of modified cottons in trimethylbenzylammonium hydroxide (Triton B). The concentration of the base used was 2.1*N*—that of maximum solvent power—and its absolute fluidity at this concentration is about 24 c.g.s. units. The same technique was used as for Triton F, but the relative inferiority of this base as a cellulose solvent is such that only the most highly degraded of the materials were completely soluble, and rate of flow measurements were therefore made only on the most degraded member of each of the six series of modified cottons. Within the experimental errors, the specific viscosities of 0.5 per cent. dispersions of all the products were identical in the two differently substituted quaternary bases Triton B and F.

Finally, measurements were made at 20° C. on 0.5 per cent dispersions in 2.5*N* sodium hydroxide solution. In order to prepare the cellulose solutions the temperature of the alkali was reduced to about -5° C.,<sup>6</sup> but even under these conditions—which are relatively very favourable to the solvent action of sodium hydroxide—the most degraded members of the series of modified cottons investigated in other solvents could not be dissolved completely in sodium hydroxide. For the study of solutions in this alkali, a number of hydrocelluloses more modified than any of those previously examined were specially prepared. They were dissolved in the alkali out of contact with air, but their viscosities were measured in a U-tube type of viscometer without special precautions to exclude air since it was found that, when solutions of such low viscosity celluloses in sodium hydroxide were allowed to stand in the open viscometer, their rate of flow only changed very slowly under the oxidative influence of the air. The ratio of the specific viscosity of these hydrocelluloses in sodium hydroxide to that in cuprammonium varied from 1.45 to 1.35 with increasing degradation.

According to the relation postulated by Staudinger, and applied by him to very dilute cellulose solutions, the ratio of the specific viscosities of the same cellulose at the same concentration in two different solvents is equal to the ratio of the mean molecular weights of the cellulose in the two solvents. The concentrations to which the Staudinger relation is generally applied are so low that the viscosity of the cellulose solution does not exceed that of the solvent by more than 20 per cent ( $\eta_{sp}$  below 0.2), and some published data are available relating the specific viscosities of cellulose measured under these conditions in different basic solvents. The measurements given in this paper for 0.5 per cent solutions of modified cottons cover a range of specific viscosity from about 1 to 10—thus much higher than that to which the



Staudinger relation is applied—and within this range no proportionality exists between specific viscosity and concentration for a given cellulose in a given solvent. Hence there are no *a priori* reasons for assuming that the ratio of the specific viscosities of 0.5 per cent dispersions in two solvents should be the same as the ratios derived from measurements at the much lower concentrations to which most previously published data refer. The comparison is nevertheless of some interest. It should be noted that whilst comparative measurements in different solvents at cellulose concentrations of 0.5 per cent. have the disadvantage that they are far removed from the theoretically ideal observations in very dilute solutions, measurements more satisfactory in this respect have the disadvantage of making greater demands on the accuracy of experimental observations in work where accurate viscometry is not easily achieved. In addition, some of the published comparisons between specific viscosities in different solvents at low concentrations have unfortunately been obtained from measurements on chemically modified celluloses of which the chemical history is inadequately specified. The importance of this lies in the fact already demonstrated that the mean chain-length of certain oxidised celluloses is diminished by the action of basic solvents, and to different extents for different solvents and different methods of oxidation.

Staudinger and Daumiller<sup>6</sup> determined the specific viscosities at low concentration of five cellulose materials in the three solvents, tetraethylammonium hydroxide, cupri-ethylenediamine and cuprammonium, all at 20° C. Four of the materials are described as bleached, less strongly bleached, strongly bleached or very strongly bleached linters or cotton, and the fifth as a cuprammonium rayon. Staudinger and Sorkin<sup>7</sup> determined the specific viscosities in sodium, lithium and cuprammonium hydroxides of dilute solutions of highly degraded materials obtained by the action of acids on "cotton wool." Table I gives the results obtained by Staudinger in the different bases, expressed as ratios to those obtained in cuprammonium

Table I

Solvent S	Specific Viscosity Ratio : Solvent S/Cuprammonium	
	At low concentration (Staudinger)	At 0.5% concentration (Present results)
Et <sub>4</sub> NOH	0.77 to 0.90 (Hypochlorite oxycelluloses ?)	—
Me <sub>3</sub> BzNOH and Me <sub>2</sub> Bz <sub>2</sub> NOH	—	0.85 to 1.05 with increasing degradation (Hypochlorite oxycelluloses) 1.55 (Hydrocelluloses)
CuEn <sub>2</sub> (OH) <sub>2</sub>	1.65, 1.57 (Hypochlorite oxycelluloses ?)	2.2 to 1.7 with increasing degradation (Hydrocelluloses and Hypochlorite oxycelluloses)
NaOH	about 1.1 (Hydrocelluloses)	1.45 to 1.35 with increasing degradation (Hydrocelluloses)
LiOH	about 1.1 (Hydrocelluloses)	—

solution, and it compares them with the specific viscosities recorded here for 0.5 per cent dispersions in different solvents at 20° C, also expressed as a ratio to that in cuprammonium.

It seems probable that the chemical modification of the materials used by Staudinger in the study of tetraethylammonium hydroxide (and cupri-

ethylenediamine) solutions was produced by the action of hypochlorite bleach liquors, and that the materials should be compared with the alkali-sensitive hypochlorite oxycelluloses of this paper, for which the specific viscosity ratios for 0.5 per cent. solutions in two other quaternary bases are similar to those obtained by Staudinger in the tetraethyl base.

So far as the limited and rather incomplete data permit, the above comparisons show that the ratio of specific viscosities in different solvents at the same cellulose concentration does not vary greatly over a wide range of concentration and specific viscosity. The most fundamental values of this ratio are those derived from alkali-insensitive modified celluloses, such as the hydrocelluloses, for which there is no reason to suppose that the average molecular chain-length is affected by reaction with the alkaline solvents employed. For these, the specific viscosity ratio is not equal to unity, the value that it would possess according to the Staudinger relation if the mean molecular weight were independent of the solvent. The divergence is not, however, to be interpreted as showing that the solvents affect the chain-length of the hydrocelluloses, but more probably that the molecular weight of the dissolved cellulose is determined, not only by the chain-length of the cellulose, but also by the formation of specific compounds or complexes between the cellulose and the solvent.

## EXPERIMENTAL

### (1) Modified and Unmodified Cottons

All modified cottons were prepared from purified cotton linters (No. 327) by the methods customary in these laboratories. The linters had been boiled with 2 per cent. sodium hydroxide under pressure and lightly bleached with hypochlorite, but the degree of chemical modification and the alkali-sensitivity resulting from the processing were both small. The fluidity of this "unmodified" material in 0.5 per cent cuprammonium solution was 5.6, rising to 6.2 after treatment with 0.1*N* sodium hydroxide for 24 hours at the room temperature. It was chemically modified as follows: (a) By the action of hydrochloric acid, 200 gm per l, for various times at 25° C: (b) By the action of the following dilute oxidising solutions for various times at 20° C.: *N*/25 potassium dichromate, *N*/5 in sulphuric acid, *N*/25 hypochlorite buffered at pH 7.5 with phosphate; *N*/100 periodic acid, and *N*/100 hypobromite, *N*/10 in sodium hydroxide: (c) By the action at 20° C. of *N*/5 oxalic acid to which various volumes of *N*/25 potassium dichromate were added in the presence of the unmodified cotton, the action being allowed to continue until the oxidising agent was completely reduced. The ratio of cotton to modifying solution was 20 gm. per l in all preparations, and after the desired treatment, the materials were well washed with water, and dried in the air. Samples taken from selected members of each series were submitted to the following alkaline treatments subsequent to modification: (1) Immersion in 0.1*N* sodium hydroxide for 24 hours at room temperature, (2) boiling with 0.25*N* sodium hydroxide for six hours at atmospheric pressure. Samples treated in this way are distinguished in the tables of results by the letters A and B respectively following the appropriate sample number.

### (2) Solvents

The Triton solvents were prepared from the commercial products referred to as Solution B in the foregoing paper.<sup>1</sup>

Cupri-ethylenediamine was prepared as follows: A solution of ethylenediamine 0.40*M* in the base was shaken for an hour with a weight of cupric hydroxide 80 per cent. in excess of that corresponding to a value of two for the molar ratio of organic base to copper hydroxide. The excess of hydroxide was filtered off, and the solution allowed to stand for some days, when a little cuprous oxide deposited, and was removed by filtration. After six days no further deposition occurred during longer standing, and the molar ratio of base to copper hydroxide was 1.88. In the method of cellulose viscometry used in these laboratories,<sup>2</sup> the mixture of cellulose and solvent is agitated by the motion of a small volume of mercury. In the presence of the mercury, a further slight precipitation of cuprous oxide occurred both from the cupri-ethylenediamine solvent alone, and from solutions of cellulose in it. When the agitation was stopped, the cuprous oxide, mixed with finely divided mercury, settled as a heavy greenish sludge, which was rapidly expelled from the viscometer when flow started, and did not interfere with the viscosity measurement.

Cuprammonium was drawn from the stock solvent used in these laboratories for the routine measurement of cellulose fluidity.<sup>2</sup>

Table II records the concentrations, densities at 20° C., and fluidities in c.g.s. units at 20° C., of the solvents used in this investigation.

Table II

Solvent	Concentration	Density	Fluidity c g s units/20° C.
Sodium hydroxide	2.50 <i>N</i>	1.098	56.7
Triton B (Me <sub>3</sub> Bz NOH)	2.13 <i>N</i>	1.048	24.1
Triton F (Me <sub>2</sub> Bz <sub>2</sub> NOH)	2.01 <i>N</i>	1.063	14.4
Cupri-ethylenediamine	0.40 <i>M</i> En, 0.213 <i>M</i> Cu	1.020	88.4
Cuprammonium hydroxide	Nominal 200 gm NH <sub>3</sub> { per 15 gm Cu { litre	Nominal 0.94	Nominal 72.1

For calculating the relative or specific viscosities of cellulose solutions in cuprammonium, the value of 72 has generally been used for the fluidity of the solvent at 20° C. Samples taken from a large laboratory stock made to the specified concentration are often found to have a fluidity exceeding this by a few per cent., on account of unavoidable loss of ammonia during storage. The error in using the nominal figure only becomes serious for low relative or specific viscosities, that is, for highly modified celluloses in 0.5 per cent solutions. The most highly modified materials concerned in this work are the hydrocelluloses HL 30, 31, 32, and SHL 11, 12 used in Table II for comparing flow properties in cuprammonium and sodium hydroxide solutions. For these, and for HL 26 in Tables I and II, the fluidity of the solvent was measured at the same time as that of the solution, and the experimental value has been used in calculating the specific viscosity. Values given for the cuprammonium solutions of other very modified cottons may be associated with appreciable errors owing to the use of a nominal value for the solvent fluidity.

### (3) Viscometry

Except for the measurements in sodium hydroxide solution, all viscosities were determined in the special type of viscometer (X-type) specified by

Chibbens and Little<sup>3</sup> for observations on cellulose solutions in cuprammonium, though for measurements in the Triton solvents the rubber stopper in the instrument as specified was replaced by a ground-in capillary stopper. The constant of the instrument is about 0.05 centistoke per sec., and the kinetic energy correction is very small for the shortest times of flow observed with the solutions in Triton F. On the other hand, the kinetic energy corrections are considerable for 0.5 per cent solutions of the highly modified materials in cuprammonium. For the most modified cottons dissolved in this solvent, a viscometer was therefore used of similar kind to that specified by Chibbens and Little, but with a longer and narrower capillary, and a constant of about 0.0125 centistoke per sec.

In the method described, the cellulose solutions are prepared in the viscometer, mixing being effected by the to-and-fro motion of a small volume of mercury in a closed system with no free air space. This procedure was found to yield a homogeneous solution after 18 hours rotation of the viscometer even from the most viscous system examined, namely, the 0.5 per cent. dispersion of the "unmodified" cotton in Triton F, it might, however, prove inadequate for intrinsically more viscous cottons in Triton F, corresponding, for example, to fluidities considerably below 1 for the 0.5 per cent. dispersion in this solvent.

For the observations on solutions of modified cotton in sodium hydroxide, the following methods were used. The dissolution vessel consisted of a glass centrifuge tube of known volume, closed by a ground-in capillary stopper. The tube containing the correct weight of cotton to yield a 0.5 per cent. solution, and a  $\frac{3}{8}$  inch steel ball, was completely filled with 2.5*N* sodium hydroxide solution to the exclusion of air, the capillary exit of the stopper then being closed. The tube was cooled for about 15 minutes in an ice-salt freezing mixture, and shaken periodically by hand, when the contents were agitated by the motion of the ball. No difficulty was experienced in obtaining virtually complete solution of sufficiently modified cottons in this way. The solution was allowed to attain room temperature, and centrifuged to remove a few fine particles that might cause trouble in the viscometer. This was a pipette-filled U-tube type with a constant of about 0.013 centistoke per sec., and a very small kinetic energy correction for the solutions examined. The clear solution was transferred to the viscometer, and its time of flow observed without special precautions to exclude air. When a 0.5 per cent. cellulose solution in sodium hydroxide of fluidity 25.1 c.g.s. units, or relative viscosity 2.26, was allowed to stand undisturbed in the viscometer overnight the increase in fluidity due to oxidation of dissolved cellulose by the air was less than 1 per cent. The fluidity of the same material in 0.5 per cent cuprammonium solution was measured by the same method in the same instrument, and the result (38.1 c.g.s. units) was substantially the same as that obtained by the standard method of measurement in a modified X-type viscometer. The fluidity of the cuprammonium solution increased, however, by over 5 per cent. when the solution stood overnight in the viscometer.

#### (4) Results

The results of rate of flow measurements at 20°C., expressed both as the fluidity in c.g.s. units and as specific viscosity, are given in Tables III and IV. Their most important features have already been discussed, and illustrated in Figs. 1 and 2.

Table III. Rate of Flow in Cuprammonium, Triton F and Cupri-ethylenediamine

Material	Sample No	Cuprammonium		Triton F		Cupri-ethylene-diamine	
		Fluidity at 20°C c g s. units	$\eta_{sp}$ 20°C.	Fluidity at 20°C c g s. units	$\eta_{sp}$ 20°C.	Fluidity at 20°C c g s. units	$\eta_{sp}$ 20°C.
Unmodified cotton	327 327/A	5.6 6.2	11.8 10.6	0.89 —	15.2 —	3.38 —	25.2 —
Hydrocelluloses	HL21	14.7	3.90	2.18	5.62	9.34	8.47
	22	20.1	2.58	2.87	4.03	13.91	5.36
	23	24.8	1.90	3.61	2.99	19.47	3.54
	24	31.1	1.31	4.81	2.00	26.6	2.33
	25	36.3	0.98	5.63	1.56	—	—
	26	38.8	0.91	6.27	1.30	—	—
	22/A	20.5	2.51	2.97	3.85	14.34	5.17
	24/A	31.1	1.31	4.78	2.01	26.7	2.31
	22/B	20.8	2.46	2.99	3.83	14.72	5.01
	24/B	31.3	1.30	4.85	1.97	26.4	2.35
Dichromate/ sulphuric acid oxycelluloses	K51	12.2	4.90	2.07	5.98	—	—
	52	17.4	3.14	2.85	4.06	—	—
	53	24.1	1.98	4.13	2.49	—	—
	54	30.5	1.36	5.35	1.70	—	—
	55	36.1	0.99	6.37	1.26	—	—
	56	40.1	0.79	7.31	0.97	—	—
	52/A	20.2	2.56	2.92	3.95	—	—
	54/A	33.7	1.14	5.29	1.73	—	—
	52/B	20.4	2.53	3.19	3.53	—	—
	54/B	33.5	2.15	5.33	1.71	—	—
Neutral hypochlorite oxycelluloses	NC21	9.6	6.50	2.27	5.36	6.01	13.72
	22	11.9	5.05	2.72	4.32	7.46	10.85
	23	15.4	3.67	3.58	3.04	10.49	7.43
	24	21.0	2.43	4.51	2.20	15.09	4.86
	25	28.0	1.57	5.56	1.60	24.2	2.66
	26	31.8	1.26	6.20	1.33	28.4	2.12
	22/A	19.2	2.75	2.96	3.87	13.78	5.41
	24/A	28.5	1.52	4.56	2.16	24.6	2.60
	22/B	19.7	2.65	2.88	4.02	14.14	5.26
	24/B	29.7	1.42	4.61	2.13	24.7	2.58
Dichromate/ oxalic acid oxycelluloses	KOX11	12.0	5.00	1.73	7.32	—	—
	12	19.2	2.75	2.72	4.31	—	—
	13	25.6	1.81	3.88	2.72	—	—
	14	30.1	1.39	4.72	2.05	—	—
	15	34.9	1.06	5.74	1.51	—	—
	16	41.2	0.75	6.73	1.14	—	—
	12/A	19.6	2.67	2.85	4.06	—	—
	14/A	30.7	1.34	4.77	2.02	—	—
	12/B	19.2	2.75	2.91	3.95	—	—
	14/B	29.7	1.42	4.76	2.03	—	—
Periodic acid oxycelluloses	P48	22.5	2.20	3.37	3.29	—	—
	49	31.8	1.26	5.04	1.87	—	—
	50	36.5	0.97	5.94	1.43	—	—
	51	12.0	5.00	1.77	7.13	—	—
	52	17.1	3.21	2.49	4.80	—	—
	54	25.0	1.88	3.81	2.79	—	—
	55	30.8	1.34	4.80	2.01	—	—
	56	35.7	1.02	5.78	1.50	—	—
	57	39.4	0.83	6.49	1.22	—	—
	48/A	20.6	2.50	3.14	3.60	—	—
	49/A	29.8	1.42	4.63	2.12	—	—
	48/B	21.1	2.41	3.04	3.74	—	—
	49/B	30.3	1.38	4.69	2.08	—	—
Alkaline hypobromite oxycelluloses	Br11	12.3	4.85	1.98	6.29	—	—
	12	19.1	2.77	2.92	3.94	—	—
	13	24.8	1.90	3.89	2.71	—	—
	14	30.6	1.35	4.92	1.93	—	—
	15	35.2	1.04	5.86	1.46	—	—
	16	38.1	0.89	6.30	1.29	—	—
	12/A	21.3	2.38	3.20	3.60	—	—
	14/A	31.7	1.27	5.01	1.88	—	—
	12/B	22.1	2.26	3.28	3.39	—	—
	14/B	32.3	1.23	5.18	1.79	—	—

**Table IV**  
**Rate of Flow in Cuprammonium, Triton B, Triton F and Sodium Hydroxide**

Material	Sample No	$\eta_{sp}$ at 20°			
		Cuprammonium	Triton B	Triton F	NaOH
Hydrocelluloses	HL26	0.91	1.28	1.30	—
	30	0.62	—	0.85	0.90
	31	0.57	—	—	0.80
	32	0.55	—	—	0.74
	SHL11	0.62	—	—	0.89
	12	0.48	—	—	0.65
Dichromate/sulphuric acid oxycellulose	K56	0.79	0.97	0.97	—
Neutral hypochlorite oxycellulose	NC26	1.26	1.28	1.33	—
Dichromate/oxalic acid oxycellulose	KOX16	0.75	1.21	1.14	—
Periodic acid oxycellulose	P57	0.83	1.26	1.22	—
Alkaline hypobromite oxycellulose	Br16	0.89	1.29	1.29	—

#### SUMMARY

The fluidities of 0.5 per cent solutions of cotton cellulose chemically modified by hydrolysis and oxidation in a variety of different ways have been compared in the two solvents cuprammonium and dimethyldibenzylammonium hydroxide (Triton F) at 20° C. There is no unique relationship between fluidities in the two solvents, but if the modified cottons are first treated with dilute alkali the relation becomes approximately independent of the method of modification, and the same as that yielded by the hydrocelluloses with or without the alkali treatment. These results are explained in terms of the alkali-sensitivity of certain oxycelluloses, which suffer a further fragmentation of chain-molecules under the influence of dilute alkalis, this effect being produced to different extents by the two basic solvents. Thus, the effect produced by the non-solvent alkali sodium hypochlorite on the products of oxidation of cotton with nearly neutral hypochlorite solutions is greater than that produced by cuprammonium, but not than that produced by Triton F. Hence for these oxidised materials the fluidities in the two solvents are functions of different chain-length distributions, though this is not the case for the hydrocelluloses and some other types of oxycellulose. The pre-treatment of all the modified cottons with dilute sodium hydroxide eliminates this difference.

The relative advantages of cuprammonium and Triton F as solvents for specifying the flow properties of celluloses are discussed. Triton F has the advantage that its degrading action on all alkali-sensitive modified cottons is similar to that of the inorganic alkalis, so that the fluidity in this solvent, unlike that in cuprammonium, is a measure of the total chemical deterioration of the cellulose, actual and latent. In order to obtain the same information from measurements in cuprammonium solution, it is necessary first to submit the material to treatment with a dilute inorganic alkali. It is, however, uncertain at present whether Triton F can be produced commercially in a sufficiently uniform quality to serve as a standard solvent.

The rate of flow measurements are also expressed in the form of specific viscosities, and the work has been extended to include measurements on modified cottons dissolved in cupri-ethylenediamine, trimethylbenzylammonium hydroxide (Triton B) and sodium hydroxide. On account of their inferior solvent power, the two latter could only be used as solvents for highly modified cottons. So far as can be seen from the somewhat inadequate published data, the ratio of the specific viscosities of 0.5 per cent. solutions of modified cottons in two different solvents is not very different from the ratio obtained at the much greater dilutions to which the Staudinger relation is generally applied. For the hydrocelluloses, the specific viscosities are not the same in the different basic solvents, being lowest in cuprammonium, and followed in order by the results obtained in sodium hydroxide, Tritons B and F (identical), and cupri-ethylenediamine (highest).

#### REFERENCES

- <sup>1</sup> Brownsett and Clibbens. Foregoing paper
- <sup>2</sup> Clibbens and Little. *Shirley Inst Mem*, 1936, 15, 25, or *J Text Inst.*, 1936, 27, 1285
- <sup>3</sup> Davidson. *Shirley Inst Mem*, 1937-38, 16, 29, or *J Text Inst*, 1938, 29, 1195.
- <sup>4</sup> Russell and Woodberry. *Ind Eng Chem, Anal Ed*, 1940, 12, 151
- <sup>5</sup> Davidson. *Shirley Inst Mem*, 1934, 13, 1, or *J Text Inst*, 1934, 25, 1174
- <sup>6</sup> Staudinger and Daumiller. *Ber. Deut chem. Ges*, 1937, 70, 2508
- <sup>7</sup> Staudinger and Sorkin. *Ber Deut chem. Ges*, 1937, 70, 1565

Received 15/1/41

# THE JOURNAL OF THE TEXTILE INSTITUTE

## TRANSACTIONS

### 7—A CORRELATION PERIODOGRAPH FOR THE MEASUREMENT OF PERIODS IN DISTURBED WAVE-FORMS

By J. G. MARTINDALE, Ph.D., A Inst.P.

(Formerly at the British Cotton Industry Research Association)

(Copyright by The Textile Institute)

#### I. INTRODUCTION AND SUMMARY

In the course of researches at the Shirley Institute photographic records were obtained of the continuous variations in a certain property of cotton. This variation had a wave-like form, and a rapid means of estimating the length of the waves was sought. The investigation thus resembles a type that has arisen in meteorology in the analysis of series of observations such as those of sun-spot activity. The chief characteristic of these series of observations is the apparent periodic nature of the variations, the sun-spot activity, for instance, appears to vary periodically with a period of about eleven years. The variation is not, however, strictly regular so that estimation of its amplitude and wave-length presents difficulties.

Measurements on such data have given rise to the conception of two types of periodicity. The first type is one in which the variations consist in part of a strictly periodic variation of constant wave-length and amplitude and, added to this, variations of random amount and occurrence which are yet of sufficient magnitude to mask the true periodicity. Harmonic analysis is the procedure adopted in order to separate the periodic from the random variations, and to determine the length of the underlying period or periods. Such harmonic analysis may be made by means of an instrument devised by Foster<sup>1</sup>.

The second type of periodicity which might give rise to such series of observations was suggested by Yule<sup>2</sup>. He pointed out that there was no reason for assuming that the nature of the variations was of the above-mentioned type, and suggested that, in the case of the sun-spot numbers at least, such data were more characteristic of an oscillating system operated on by some external disturbing force, like "a pendulum subjected to successive small random impulses". This would give rise to oscillations of continually altering amplitude and phase, and he showed that harmonic analysis of such a wave motion gives results which may be misleading and subject to a large error, because the length of the wave is now a variable quantity, and harmonic analysis, in effect, splits up the variation into simple harmonic components. Yule showed that the results of his investigations on the sun-spot numbers were more in agreement with this idea of an oscillating system affected by disturbing forces than with that of strictly



periodic variations with superimposed random fluctuations. A series of observations of an oscillation of this kind is referred to as a disturbed series.

The method employed by Yule for the analysis of disturbed series involved the calculation of what are termed serial correlation coefficients. If the series consists of observations  $u_1, u_2 \dots u_n$  at equal intervals of  $t$ , then the observations  $u_1, u_2 \dots u_{n-s}$ , and the observations  $u_s, u_{s+1} \dots u_n$  are written in adjacent columns, and the correlation coefficient between these two series is calculated in the usual way. By taking different values of  $s$  from 1 to  $s$  a set of serial correlation coefficients  $r_1, r_2 \dots r_s$  are obtained. Now if the  $u$ 's tend to vary periodically with a period,  $\lambda$ , the mean length of the disturbed period will tend to approach  $\lambda$  if the observations are sufficiently extended to contain a large number of periods, moreover, for values of  $s$  equal to 0,  $\lambda$ ,  $2\lambda$ , etc., the value of  $r_s$  will have its greatest positive value, while if  $s = \lambda/2$ ,  $3\lambda/2$ ,  $5\lambda/2$ , etc.,  $r_s$  will have its greatest negative value. Plotting  $r_s$  against  $s$  therefore gives a curve, called the "correlation periodogram", which exhibits a periodicity of the same length as that in the original observations, but, since each point on it is a value of  $r$  calculated from the whole series of original  $u$ 's, it is much smoother than the curve showing the variation of  $u$  as a function of  $t$ . The advantage of the correlation periodogram for the analysis of disturbed series is that unlike the ordinary method of harmonic analysis, it is not affected by the total disturbance of the wave over the whole range of the observations, the correlation is reduced only by the disturbances that occur within the comparatively short range  $s$ . The method has been used by Walker<sup>3</sup> who discusses it at length in his paper.

The purpose of the present paper is to describe an instrument for recording the correlation periodogram when the original observations are supplied in a suitable form without having to compute correlation coefficients arithmetically. This instrument is called the "Correlation Periodograph", the principle on which it works, the method of its construction, and its application are described. Although it has been developed for the purpose of examining periodic variation in the products of cotton spinning, it would be applicable equally to the determination of lengths of periods in any series of observations of the kind mentioned. It has, in fact, been so used in a check of its performance on the series of sun-spot numbers<sup>2</sup> and on weather data<sup>3</sup> (Records of pressure variation at Port Darwin) for which the results of independent arithmetic computation have already been published.

## II. PRINCIPLE OF THE METHOD OF RECORDING THE CORRELATION PERIODOGRAM

The series of observations to be examined are arranged in graphical form showing the value of  $u$  as ordinate plotted against the other co-ordinate, say time  $t$ , giving a trace such as is shown in Fig. 1. The area above the curve is blackened, and the curve then photographed on a process plate at two different magnifications, from which two positives of different sizes, A and B, are made, B being the smaller (Fig. 2). These photographs are made clear in the transparent parts, and as in determining the length of a period only the variation of  $u$  is of any moment, the sensitivity of the subsequent measurement is increased by blocking out all the transparent part of the curve below the level of the lowest trough, leaving the clear part of the photographs to represent the variation of  $u$ .

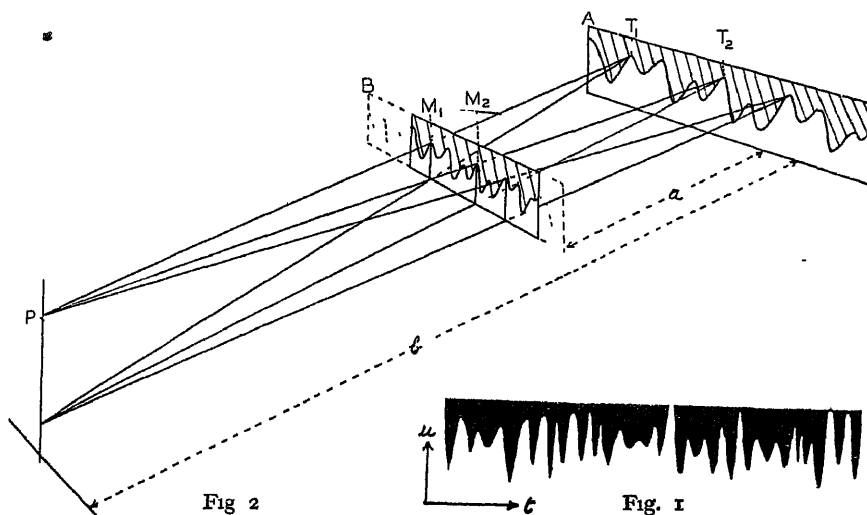


Fig 2

Fig. 1

The Correlation Periodogram

Plates A and B are mounted in the instrument parallel to one another at a distance  $a$  apart (Fig 2); a source of diffuse light is placed behind the photograph A so that rays of light spread out uniformly in all directions from its transparent parts. Fans of rays through corresponding ordinates on the two curves, such as those at  $T_1$  and  $M_1$ ,  $T_2$  and  $M_2$ , Fig. 2, all intersect on a line through P parallel to the direction of the ordinates and distant  $b$  from A, where  $b/(b-a)$  ( $=c$ ) is the ratio of the scales of curve A to curve B. If the heights of the ordinates of curve B are represented by  $u_1, u_2, u_3, \dots, u_n$ , the heights of corresponding ordinates of curve A are  $cu_1, cu_2, cu_3, \dots, cu_n$ . The amount of light transmitted by an element of the curve A, of width  $\delta t$  and height  $cu_1$  is proportional to  $cu_1\delta t$ , and of this an amount proportional to the corresponding ordinate  $u_1$  on curve B falls on the line through P, so that the amount of light transmitted by the element of curve A and falling on the line through P is proportional to  $cu_1^2\delta t$ .

The total amount of light  $I_0$  falling on the line P due to all the observations  $u_1, u_2, \dots, u_n$  is proportional to  $\sum_{i=1}^n u_i^2\delta t$ . We may therefore write

$$I_0 = K \sum_{i=1}^n u_i^2\delta t. \quad (1)$$

where  $K$  is a constant

If curve B is traversed a distance  $s$  along its own length, the amount of light,  $I_s$ , falling on P is similarly given by

$$I_s = K \sum_{i=1}^n u_i u_{i+s} \delta t \quad \dots \dots \dots (2)$$

If  $y_i$  is the deviation of  $u_i$  from its mean value,  $\bar{u}_0$ , over the observations from 1 to  $n$ , and  $y_{i+s}$  is the deviation of  $u_{i+s}$  from its mean value,  $\bar{u}_s$ , over the observations from  $1+s$  to  $n+s$

Then

$$\begin{aligned} I_s &= K \cdot \delta t \sum_{i=1}^n (\bar{u}_0 + y_i)(\bar{u}_s + y_{i+s}) \\ &= K \cdot \delta t \sum_{i=1}^n (\bar{u}_0 \bar{u}_s + y_i y_{i+s}) \dots \dots \dots (3) \end{aligned}$$

since  $\sum_{i=1}^n y_i$  and  $\sum_{i=1}^n y_{i+s}$  are each zero.

The coefficient of correlation between  $u$ 's separated by  $s$  intervals is

$$r_s = \frac{\sum_{l=1}^n y_l y_{l+s}}{n \sigma_0 \sigma_s}$$

where  $\sigma_0$  and  $\sigma_s$  are the standard deviations of  $y_1$  to  $y_n$  and  $y_{1+s}$  to  $y_{n+s}$  respectively.

$$I_s = nk\delta t(\bar{u}_0 \bar{u}_s + r_s \sigma_0 \sigma_s) \quad \dots \dots \dots (4)$$

If  $s$  is small compared with  $n$ ,  $\bar{u}_s$  and  $\sigma_s$  only vary slightly as  $s$  varies, and

$$I_s = C_1 r_s + C_2 \text{ (very nearly)} \quad \dots \dots \dots (5)$$

where  $C_1$  and  $C_2$  are constants.

Thus the variation of  $I_s$  as the curve B is traversed is proportional to the variation of  $r_s$ , so that by measuring this light variation the correlation periodograph may be obtained (Fig. 8). This has a maximum value  $I_0$  ( $r=1.0$ ), when  $s=0$ , and a series of smaller maxima as  $r_s$  fluctuates. The periodogram ought to be nearly symmetrical about the central maximum ( $s=0$ ) since

$$r_s = \frac{\sum_{l=1}^n y_l y_{l+s}}{n \sigma_0 \sigma_s} \quad \text{and} \quad r_{-s} = \frac{\sum_{l=1}^n y_l y_{l-s}}{n \sigma_0 \sigma_{-s}},$$

and these are nearly equal if  $s$  is small compared with  $n$ .

It may be noted that if the curves A and B represent the function  $u=\varphi(t)$ , and curve A extends from  $t=0$  to  $t=T$ , we have, in general, instead of equation (2),

$$I_x = K \int_0^T \varphi(t) \varphi(t+x) dt \quad \dots \dots \dots (6)$$

where  $x$  is the value of the displacement of the curve B from the central position,  $K$  is an instrument constant.

In the correlation periodograph a photo-cell is used to measure the variation in the amount of light transmitted through a slit parallel to the ordinates of the curves in A and B (i.e. a vertical slit through P), as the curve B is traversed across the apparatus. The slit must obviously be long enough to collect all the light from the maximum ordinate of curve A which is transmitted by the corresponding ordinate of curve B. The correlation periodogram is obtained by plotting the photoelectric current against the position of plate B, the length of any period in the periodogram is then given in the units of  $t$  measured on the scale of plate B.

### III. CONSTRUCTION OF THE CORRELATION PERIODOGRAPH.

The instrument is shown diagrammatically in Fig. 3 both in elevation with the side panel removed, and in plan with the top removed. It consists essentially of (1) Light source, (2) Plate-holders, (3) Slit; and (4) Means for measuring the light incident on the slit.

(1) *Light source.* As a source of illumination five 60-watt opal lamps,  $2\frac{1}{2}$ " wide and 3" tall, are arranged as shown in a white box in front of the brass plate  $D_1$ , these lamps give a reasonably uniform source, as the amplitude of the curve A was never more than about 1", though, if necessary, sheets of ground glass could be interposed to increase the uniformity of the illumination.

(2) *Plate-holders* A brass plate  $D_1$  has a rectangular aperture  $8'' \times 1\frac{3}{4}''$  cut in it; clips behind  $D_1$  hold the photographic plate A ( $8\frac{1}{2}'' \times 2\frac{1}{8}''$ ) on which the record of observations has been photographed. A second brass plate  $D_2$ ,

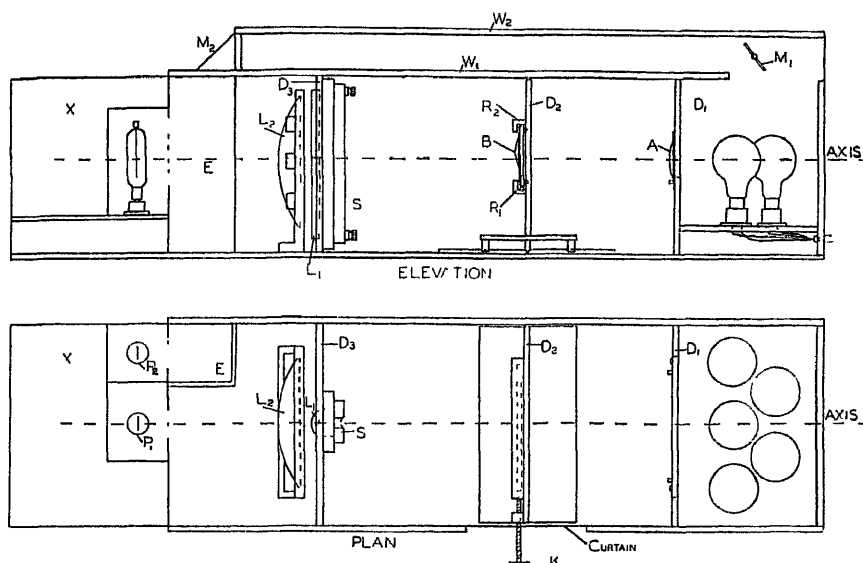


Fig. 3. Plan and Elevation of Correlation Periodograph

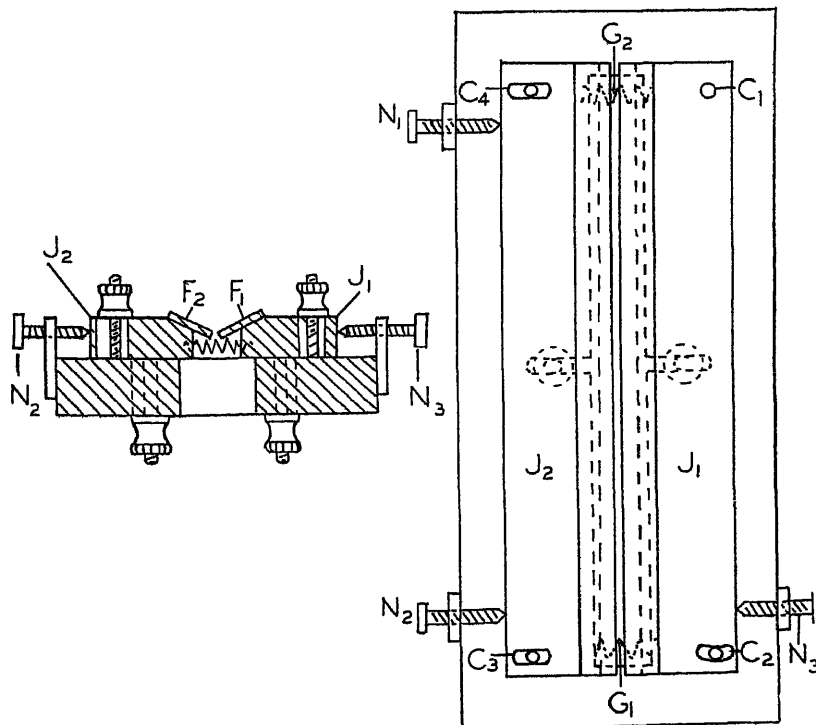


Fig. 4. Construction of Slit of Periodograph

having also a rectangular aperture and a holder for the photographic plate B, is mounted on geometric slides so that  $D_2$  is free to be moved along the axis of the instrument for adjusting the distance  $a$ . The plate-holder is mounted on the face of  $D_2$  and by rotating the screw head K its movement across the aperture in  $D_2$  can be controlled accurately. This holder is also designed on kinematic principles; it is held by springs against three steel balls set in the face of  $D_2$  and runs over two balls in the runner  $R_1$  against which it is held by a spring in  $R_2$ . It is held against the screw K by springs so that it follows the motion of the screw smoothly and without backlash.

(3) *Slit.* A wooden partition  $D_3$ , parallel to  $D_1$  and  $D_2$  at a distance  $b = 24\frac{1}{2}$ " from  $D_1$ , divides the apparatus into two compartments; over a rectangular hole in  $D_3$  is mounted the slit, S. This slit is 20 cms long and 0.33 mm wide, and is obtained by setting two steel jaws parallel to one another as shown in Fig. 4. A steel plate ( $10" \times 4" \times \frac{3}{4}"$ ) has a rectangular hole cut in it centrally and on it are mounted the two steel jaws  $J_1$  and  $J_2$ , bearing two steel strips,  $F_1$  and  $F_2$ . These have accurately ground edges to form the edges of the slit itself, and are tilted to avoid disturbing reflections of light.  $J_1$  and  $J_2$  are each clamped to the base plate by three clamping nuts, two in front and one behind, which allow the edges of the jaws to be set with respect to one another. They are pressed apart by two fairly strong springs  $G_1$  and  $G_2$  set in recesses, and are brought together by set screws  $N_1$ ,  $N_2$ ,  $N_3$  attached to the base plate. The jaw  $J_1$  is located by a threaded rod passing through the hole  $C_1$ . The set screw  $N_3$  and the slot  $C_2$  through which a threaded rod passes, allow the edge of  $F_1$  to be set vertically before the three clamping nuts are finally tightened. Then jaw  $J_2$  is slid up to  $J_1$ , slots  $C_3$  and  $C_4$  allowing sufficient movement, and by means of the set screws  $N_1$  and  $N_2$  the edge of  $F_2$  is set parallel to that of  $F_1$  at the required distance from it, and jaw  $J_2$  is then clamped tightly to the base plate by the three clamping nuts.

Accurate setting of the two jaws was ensured by observing the edges with a microscope. After the initial setting, the uniformity of the slit was measured, and further improved by rubbing down the projecting parts of the edges of  $F_1$  or  $F_2$  with fine carborundum. The slit was then set to 0.33 mm. and measured at 18 successive points 1 cm. apart. The maximum divergence from the mean width was 2 per cent.

Stray light from A is prevented from reaching the slit round the edges of  $D_2$  by black cloth pads on these edges.

The slit when mounted on the board  $D_3$  (Fig. 3) is on the axis of the apparatus, and the position of  $D_2$  is so arranged that  $b/(b-a)$  equals the ratio of the size of curve A to curve B.

(4) *Measurement of light incident on the slit.* The light incident on the slit is concentrated by lenses on to a photo-cell,  $P_1$ ; and a beam compensating for fluctuations in the source of light falls on a second photo-cell  $P_2$ , the photoelectric currents from these two cells are amplified and their difference measured by means of the well-known bridge circuit used by Wynn-Williams and others<sup>4</sup>. The photoelectric cells are of the caesium-coated vacuum type (Osram C.M.V.6), being the most sensitive for light from electric lamps and giving a current output strictly proportional to the amount of light incident upon them.

A cylindrical lens  $L_1$  (Fig 3) of the same length as the slit, and focal length 2.5 cm, is mounted immediately behind the slit with its focal line approximately coincident with it. Behind this again is a convex lens  $L_2$  with an aperture of 6" and focal length 8". These two lenses are placed so as to concentrate the light passing through the slit on to as small an area as possible—less than the area of the photo-cell  $P_1$ , used to measure the light. Lenses of ordinary quality suffice as they are not required to form sharp optical images.

A wooden board  $W_1$  forms a roof for this part of the apparatus from  $D_1$  to the box X, containing the amplifying circuit for the photoelectric currents; a second wooden board  $W_2$ , above  $W_1$ , completes an enclosure for an alternative path from the light source, needed for the compensating beam mentioned above

It has been shown (Equation 5) that the amount of light falling on the slit is  $I_s = C_1 r_s + C_2$ , i.e., it consists of two parts, a variable amount,  $C_1 r_s$ , and a constant amount,  $C_2$ , which is usually the greater part. It is the variation in  $C_1 r_s$  which has to be measured in plotting the correlation periodogram, but if the mains voltage of the source of light is unsteady, fluctuations in the total amount of  $I_s$  may at times be quite large compared with  $C_1 r_s$ . To compensate for these fluctuations, the second photo-cell,  $P_2$ , is illuminated from the same source by a second beam of light which does not pass through the curves under examination, but is directed by reflectors  $M_1$  and  $M_2$ .  $M_1$  is of tin plate, polished on one side, and painted white on the other; in an experiment, it is rotated until the amount of light falling on  $P_2$  is practically equivalent to the constant portion of light,  $C_2$ , incident on  $P_1$ . Reflector  $M_2$  sends the light into a box E having white walls, a hole in which permits scattered light to reach the photo-cell  $P_2$ . The two cells therefore receive light simultaneously from the same source, and each is kept entirely free

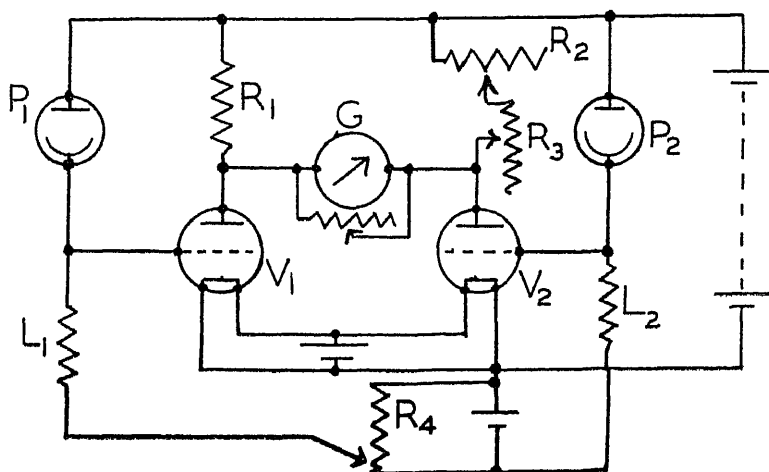


Fig 5 Photo-electric Cells and Amplifying Circuit of Correlation Periodograph.

from any light affecting the other. They are contained inside the box X, in two separate tin boxes, holes in which allow the beams of light to fall on the photo-cells. The instrument as a whole is boxed in to exclude any light from the surroundings

Two matched triodes (Osram L.P.2),  $V_1$  and  $V_2$ , Fig. 5, are used in a Wheatstone bridge circuit (Fig. 5), where the necessary particulars are given. The resistances  $R_2$  and  $R_3$  are adjusted so that when no light is incident on the photo-cells the galvanometer  $G$  shows no deflection. On switching on the lamps the reflector  $M_1$  is adjusted until the galvanometer again shows no deflection. The screw head  $K$  is then turned and as this traverses the plate  $B$ , the amount of light falling on  $P_1$  varies. The deflections of the galvanometer are proportional to the changes, and plotting the galvanometer readings against the position of the curve  $B$  as shown by the graduations on the screw head gives the correlation periodogram.

With the two matched valves in the Wheatstone bridge circuit, any change in battery voltage affects each arm of the bridge equally, consequent changes in anode currents are the same in both halves of the circuit, and the current through the galvanometer is not affected. As there is usually some small difference between the valves, they are matched more closely by making small alterations of grid bias of one of them by means of a potentiometer,  $R_4$ , of 20,000 ohms. This method of balancing results in greater steadiness of the galvanometer spot and permits the use of the two photo-cells in the way described. The grid voltages of  $V_1$  and  $V_2$  in the balanced condition are chosen so that the valves are working on the straight parts of their characteristics, so that any variation in grid voltage produces a proportional change in anode current.

#### Measurement of Absolute Values of Correlation Coefficient.

The instrument when used as described above gives the variation of correlation coefficient without determining any actual values, this being all that is required for the determination of the lengths of periods in any disturbed series, as can be seen in Fig. 8. However, the actual value of the correlation coefficient at any point on the curve may be obtained by making further measurements. For this purpose, as the scale is linear, it is sufficient to find the value of the correlation coefficient at any one point say  $Q$  on the curve (Fig. 8) other than the central peak, where  $r=1$ . The procedure is based on Equation 4. For point  $Q$ , this gives us, writing  $T$  for  $n\delta t$ , the length of the curve at  $A$ ,

$$I_Q = KT(\bar{u}_0\bar{u}_q + r_0\sigma_0\sigma_q)$$

$$\text{whence } I_0 = KT(\bar{u}_0^2 + \sigma_0^2)$$

and

$$r_q = \frac{I_Q - KT\bar{u}_0\bar{u}_q}{KT\sigma_0\sigma_q}$$

$$= \frac{I_Q - KT\bar{u}_0^2}{I_0 - KT\bar{u}_0^2} \quad \text{very nearly.}$$

Hence it is required to measure  $I_0$ ,  $I_Q$  and  $KT\bar{u}_0^2$ . To do this, the compensating beam of light is obscured and  $I_0$  and  $I_Q$  determined from the galvanometer deflections  $\theta_0$  and  $\theta_Q$ , due to the whole of the light falling on the slit when curve  $B$  is in the central position and in the position corresponding to point  $Q$  respectively.

To determine  $KT\bar{u}_0^2$ , the curve  $A$  is removed from the apparatus and replaced by a rectangular aperture of the same length  $T$ , and of constant width  $cu_0$ ; the galvanometer deflection  $\theta_1$  then observed is proportional to an amount of light  $I_1$  incident on the slit. The curve  $B$  is next removed and replaced by a long rectangular aperture of width  $u_0$ , the galvanometer deflection  $\theta_2$  now observed is proportional to an amount of light  $I_2$ .

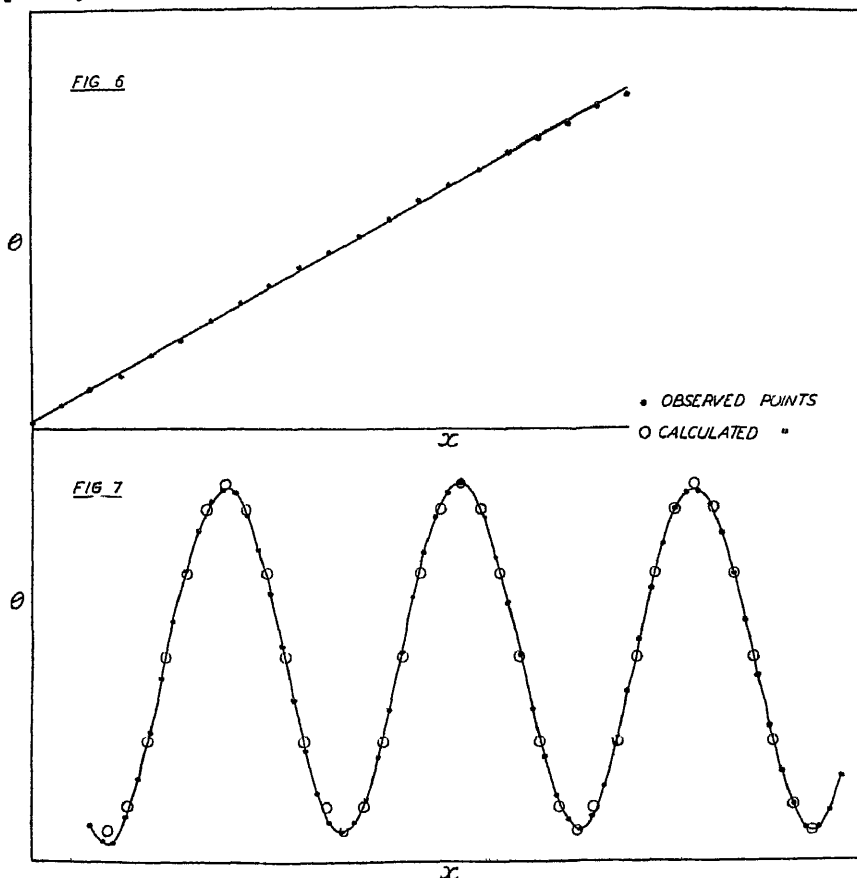
$$\text{Since } I_1 = K \sum_{i=1}^n u_0 u_i \delta t = KT u_0 \bar{u}_0$$

$$\text{and } I_2 = K \sum_{i=1}^n u_0^2 \delta t = KT u_0^2$$

$$\therefore KT \bar{u}_0^2 = \frac{I_1^2}{I_2}$$

$$\text{and } r_q = \frac{I_0 I_2 - I_1^2}{I_0 I_2 - I_1^2} = \frac{\theta_0 \theta_2 - \theta_1^2}{\theta_0 \theta_2 - \theta_1^2}$$

Some uncertainty is attached to this determination of  $r_q$  because the compensating beam of light is dispensed with, and consequently variations in lamp brightness may lead to errors in  $I_0$ ,  $I_1$ ,  $I_2$ , with consequent error in  $r_q$ , especially as this depends on the difference of the products of the possibly erroneous terms.



Figs. 6 and 7

As the apparatus has so far only been required for the determination of period length, no attempt has been made to increase its accuracy for absolute measurements of  $r$ . If this were desirable a null method similar to that adopted by T. S. Gray<sup>6</sup> in his photo-electric integrator would be suitable, the variation in the light falling on the slit being measured by so varying an aperture controlling the intensity of the compensating beam that the galvanometer shows no deflection, the size of the aperture is then a measure of the light falling on the slit.



#### IV. THE APPLICATION OF THE CORRELATION PERIODOGRAPH.

The first measurements made with the instrument were designed to show that it was functioning satisfactorily.

It has been shown (page 174) that if the form of the curve examined is  $u = \varphi(t)$  then the instrument measures the variations in an amount of light

$$I_x = K \int_0^x \varphi(t) \varphi(t+x) dt \quad \dots \dots (6)$$

The instrument may be tested by reference to a form of the function for which the variation of this integral with  $x$  is easily calculable

Two cases were examined, first the straight line  $u \equiv \varphi(t) = mt$ , and secondly a periodic curve  $u \equiv \varphi(t) = t$  from  $t=0$  to  $\pi/2$ , and  $u \equiv \varphi(t) = \pi - t$  from  $t=\pi/2$  to  $\pi$ , thus being repeated so that it is of the form of a sequence of equal triangles set corner to corner on a base line, and has a periodicity equal to  $\pi$

In the first case,

$$I_x = K \int_0^x mt \cdot m(t+x) dt$$

$$\therefore \theta = \frac{1}{3} K_1 m^2 T^3 + \frac{1}{2} K_1 m^2 T^2 x \quad \dots \dots (7)$$

The galvanometer deflection  $\theta$  should therefore vary in a linear manner with  $x$ .

In the second case  $\varphi(t)$  can be expressed as a Fourier Series

$$u \equiv \varphi(t) = \frac{\pi}{4} - \frac{8}{\pi} \left( \frac{\cos 2t}{2^2} + \frac{\cos 6t}{6^2} + \frac{\cos 10t}{10^2} + \dots \dots \right) \dots \dots (8)$$

The corresponding integral can be evaluated for this and is found to be a constant part plus an amount proportional to

$$\left( -\frac{\cos 2x}{2^4} + \frac{\cos 6x}{6^4} + \frac{\cos 10x}{10^4} + \dots \dots \right)$$

The photographs corresponding to these two functions were prepared, and measurements made on each in turn with the results shown in Figs 6 and 7, respectively. In both cases there is very close agreement between the theoretical form and that given by the instrument.

The apparatus has been applied to the determination of lengths of periods in series of disturbed observations. For instance, Fig 1 is a curve showing a harmonic variation disturbed in such a way that its amplitude and wave-length are widely variable. This curve was obtained artificially by increasing or decreasing the wave-length of a simple harmonic function according to the throw of two dice. The amplitude was also altered in random fashion. The correlation periodogram obtained from this is that shown in Fig. 8 and from it an estimate of the mean wave-length can be made. The distances of the three peaks from the central peak are as follows:—

L H S mms		R.H.S. mms		Mean		Wave-length, in mms.
6.20	..	6.60	..	6.40	..	6.40
11.80	..	12.20	..	12.00	...	6.00
18.60	..	19.20	..	18.90	...	6.30

$\therefore$  Mean wave-length = 6.23 mms

The measurement is made on 23 periods and measuring the total length of these in Fig. 1 and merely dividing by 23 gives 6.15 mms. In view of

this agreement it might seem to entail unnecessary labour to obtain the correlation periodogram, but many cases arise where the counting of the peaks in the original curve becomes quite an arbitrary matter and the existence or not of some peaks becomes a matter of personal judgment. In cases of this kind the periodogram method is essential.

The instrument has also been tested by reference to two practical cases which have been the subject of arithmetical computation. These cases are (1) Wolfer's sun-spot numbers for which Yule<sup>2</sup> calculated the wave-length from the shape of the correlation periodogram in the neighbourhood of the central maximum; and (2) atmospheric pressure variations at Port Darwin, for which Walker<sup>3</sup> computed the correlation periodogram arithmetically.

With the correlation periodograph, the periodogram for sun-spot numbers was obtained as far as the first maximum on both sides of the central maximum; this gave for the value of the period 10.7 years, compared with Yule's value of 10.6 years. The correlation periodogram for the pressure measurements at Port Darwin was continued as far as four wave-lengths on each side of the central maximum and gave a mean wave-length in the observations of 11.3 quarters, compared with Walker's value of "about 11½ quarters". Thus in both cases the agreement between the results of computation and those obtained by the instrument is very satisfactory.

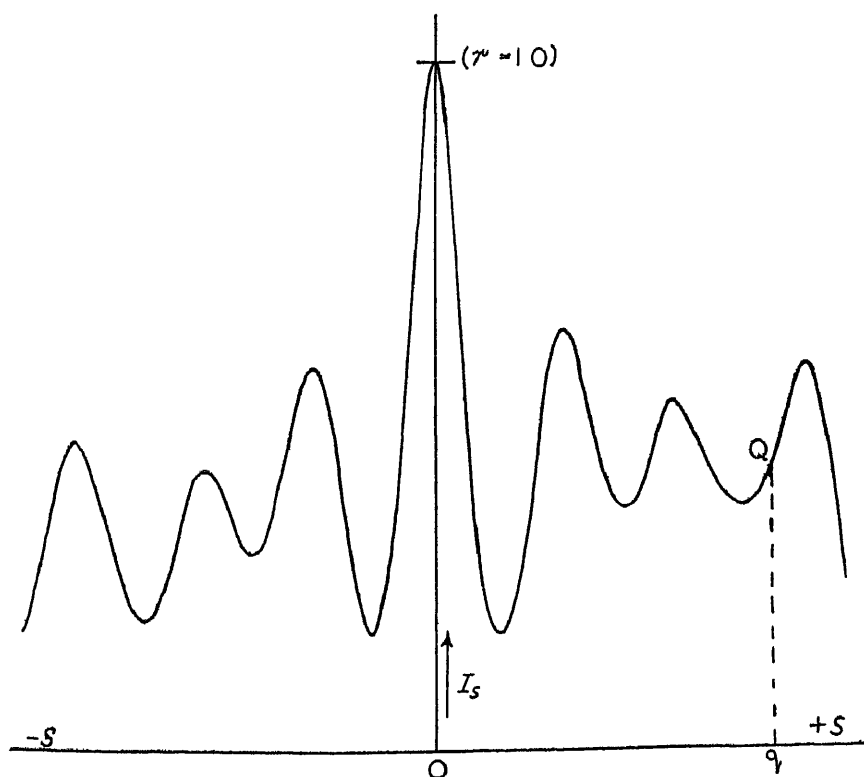


Fig. 8. Correlation Periodogram of Data of Fig. 1

## REFERENCES

- <sup>1</sup> Foster, G. A. R. *Shirley Inst Mem*, 1929, 8, No 8; *J Textile Inst*, 1930, 21, 118-28  
<sup>2</sup> Yule, G. Udny. *Phil. Trans. Roy. Soc. A.*, 1927, 226, pp 267-298.  
<sup>3</sup> Walker, Sir George *Proc. Roy. Soc., A.*, 1931, 131, p 518  
<sup>4</sup> Wynn-Williams, C. E. *Phil Mag.*, 1928 [vii], 6, p 324  
<sup>5</sup> Gray, T. S. *J Franklin Inst*, 1931, 212, p.77.

Received 7/5/41

# THE JOURNAL OF THE TEXTILE INSTITUTE

## TRANSACTIONS

### Mather Lecture

#### 8—THE CHEMISTRY OF WOOL AND RELATED FIBRES

By J B SPEAKMAN, D Sc., F I C, F.T.I

(Textile Chemistry Laboratory, Leeds University)

In the interval between two world wars, knowledge of wool and wool textile processes has advanced from a state of simple empiricism to one of scientific precision, accompanied by the development of new machinery and processes, new finishing agents, auxiliary products and dyes. These changes, and the simultaneous synthesis of fibres simulating some of the properties of wool, have given the scientist an established place in the wool textile industry. Unfortunately, the industrial significance of such developments, and their bearing on the general and technical education of the future industrialist, are as yet appreciated only by the very few. Bearing in mind the avowed purposes of the Textile Institute, and the extreme need in post-war years of combining craftsmanship, inventiveness and scientific knowledge to the advantage of the textile industry, it seems proper to devote this Mather Lecture to a summary of recent advances in the chemistry of animal fibres and their technical significance.

#### The Constitution of the Keratin Molecule

Throughout the period under review, it has been taken as axiomatic, by chemist and physicist alike, that the attempt to perfect old and develop new processes must be based on an exact knowledge of the constitution, properties and reactivity of the wool fibre. In his approach to the problem, the chemist was soon in difficulty on account of the variable composition of wool. Elementary analysis of a wide range of wools showed that their nitrogen<sup>1</sup> and sulphur<sup>2</sup> contents, particularly the latter, were distinctly variable, the single staple varies in sulphur content along its length,<sup>3</sup> according to the nutritional value of the pasture at the time each section was grown; and the single fibre is composed of three types of cell, possessing different compositions.<sup>4</sup> The impression left by such analytical work was one of baffling confusion, but a skeleton structure of the wool molecule, capable of reconciling variations in composition, was developed by X-ray<sup>5</sup> and physico-chemical<sup>6</sup> methods. This structure is shown in Fig 1. It possesses three main features, the peptide chain, the cystine linkage and the salt linkage, which receive separate discussion below.

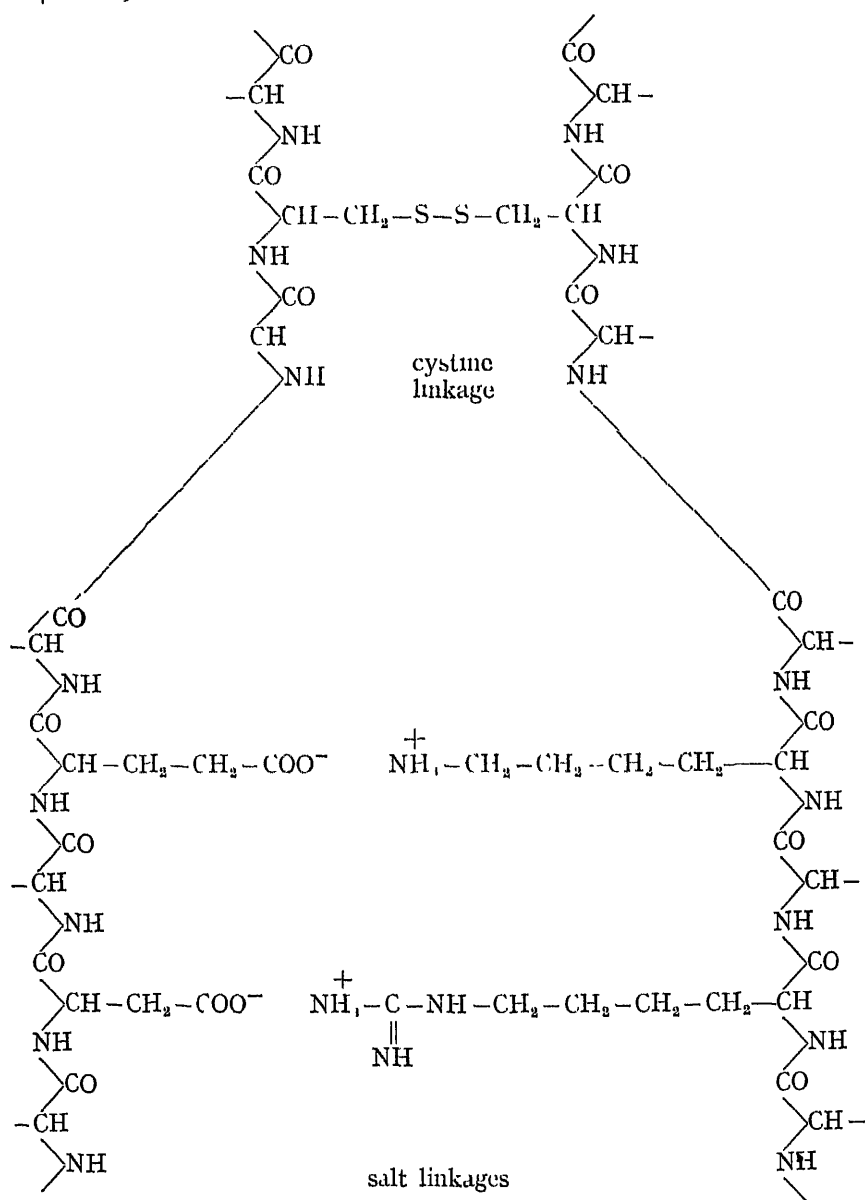
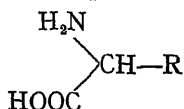
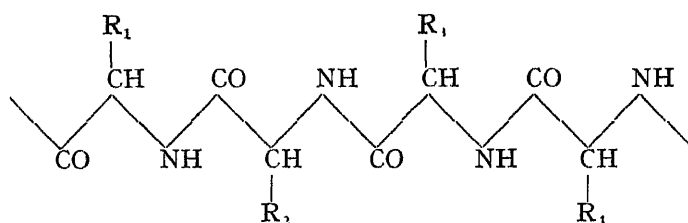


Fig. 1

(a) *The peptide chain* When wool is boiled in 20 per cent hydrochloric acid for several hours, the fibres dissolve to give a solution containing seventeen amino acids, all of which possess the same general formula.—



The acids, which differ from one another only as regards the nature of the side chain  $R$ , are known to be capable of reacting with one another to form long peptide chains of the following type.—



Compounds containing up to nineteen amino acids united in this way have been synthesised in the laboratory,<sup>7</sup> and the main peptide chains of wool appear to be of a similar character, except that they are believed to contain as many as 576 amino acid residues. During recent years, the belief has developed that the main peptide chains of proteins in general are built up according to some definite plan, and that the different amino acids, characterised by the different side chains  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ , etc., occur in a regular order. Restricting their attention to amino acids which can be estimated with a fair degree of precision, Bergmann and Niemann<sup>8</sup> were able to show that the frequency of occurrence of different amino acid residues in the peptide chains of proteins such as cattle fibrin, cattle haemoglobin and egg albumin may be expressed in the form  $2^n 3^m$ , where  $n$  and  $m$  are integers. Further, by calculating the LCM of the several frequencies, the minimum number of amino acid residues in the peptide chain, and hence the minimum molecular weight, can be found. In the case of egg albumin, the minimum number of residues was found to be 288, and when this is multiplied by the average residue weight of 124, the minimum molecular weight is found to be 35,712, in good agreement with Svedberg's value of 34,500. The possibility of applying these observations to wool has been examined by Astbury,<sup>9</sup> who, in a recent paper, indicates the composition of wool by expressing the frequency of occurrence of different amino acids in terms of numbers which conform with the Bergmann-Niemann rule, as shown in Table I.

Table I

Amino acid	Proposed numbers of residues of each amino acid in a total of 576
Glycine	64
Alanine ..	32
Valine	24
Leucine, etc	64
Phenylalanine	16
Proline	36 (or 32)
Methionine	3
Cystine/2 .	72 (or 64)
Serine	64
Threonine	32
Tyrosine	16
Tryptophane .	6
Aspartic acid	32
Glutamic acid	64
Arginine .	36 (or 48)
Lysine	12
Histidine	3
<b>TOTAL</b>	<b>576</b>
Residues as amides	64
Average residue weight	118
Molecular weight	68,000

There is, however, a difficulty in accepting this position, because, as has already been mentioned, the wool fibre is not a homogeneous structure. Besides being composed of three types of cell (two in the case of non-medullated fibres), the fibre varies in composition along its length, and contains an intercellular phase which is deficient in sulphur.<sup>10</sup> It seems, in fact, to be a mixture of proteins, to which the Bergmann-Niemann rule can hardly apply. Apparent agreement with the rule is, perhaps, to be explained in terms of Neuberger's comment<sup>11</sup> that "assuming the possibility of an error of 6 per cent (in the determination of individual amino acids in a protein) calculation indicates a very high degree of probability (approximately 80 per cent) that a purely random distribution of amino acids gives values in apparent conformity with the formula of the frequency hypothesis." Despite these difficulties, the crystallinity of the proteins indicates that the amino acids are introduced into the main peptide chains according to some definite plan. Perhaps certain amino acids are interchangeable in function, a provision which would accommodate variations in composition of the protein. Once this possibility is invoked, however, the Bergmann-Niemann rule becomes inoperative.

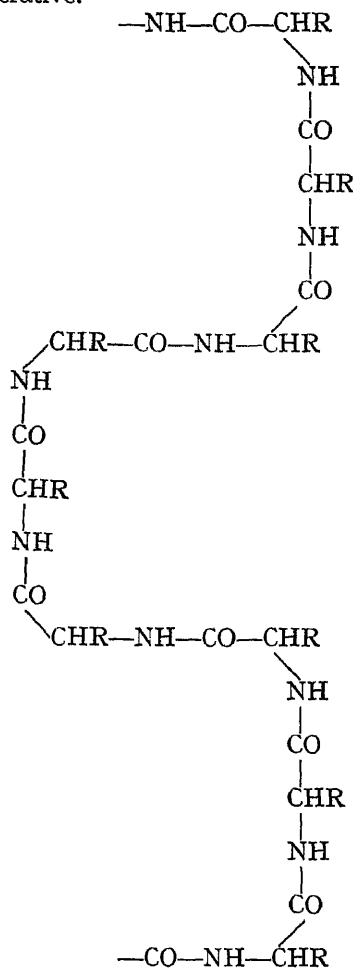
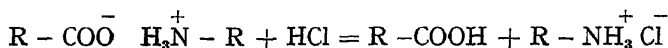


Fig 2

Besides being bent, as shown in Fig 1, in order to accommodate side chains and cross-linkages of varying length, the main peptide chains of wool are folded at right-angles to the plane of the figure. The existence of the fold was discovered by Astbury,<sup>5</sup> using X-ray methods, but the scheme of folding first proposed has been revised recently<sup>9</sup> to meet the criticisms of Neurath<sup>12</sup> and Pauling and Niemann.<sup>13</sup> The nature of the new fold is shown in Fig 2.

It gives fairly close packing of the side chains, and conforms with the known X-ray data and physical properties of the fibre.

(b) *The salt linkages* Since wool contains di-amino (lysine and arginine) and di-carboxylic (aspartic and glutamic) acids, the main peptide chains of the fibre must carry acid and basic side chains. The fact that the free acid and basic side chains are equivalent was first deduced from a study of the elastic properties of wool fibres in solutions at different pH values.<sup>14</sup> In unbuffered solutions, the resistance of fibres to extension at 22.2° C was found to be independent of pH between pH 4 and 8, and, in buffered solutions, between pH 5 and 7. Further, there was a linear relationship between the amount of acid combined with wool and the reduction in the resistance to extension. Since the whole of the acid combined with wool at pH 1 can, in the case of strong acids like hydrochloric acid, be accounted for in terms of the arginine, lysine, and histidine content of the fibre, it seemed probable that the basic side chains of these amino acids are combined with the acid side chains of dicarboxylic acids to form the salt linkages shown in Fig 1. According to this hypothesis, the attraction between the positive and negative ions of salt linkages impedes fibre extension in water by opposing unfolding of the main peptide chains. In acid solution, however, the salt linkages are broken in accordance with the following equation —



and fibre extension is facilitated. Similarly, the salt linkages are broken in alkaline solution —



and extension is facilitated, but complications arise from the simultaneous hydrolysis of cystine linkages. The range and location of the pH-stability region (pH 4 to 8 in unbuffered solutions) are therefore determined by the properties of the salt linkages. If free acid side chains were present in excess of what are required to combine with basic side chains, the pH-stability region would disappear because, as in the case of gelatin,<sup>15</sup> the free carboxyl groups would begin to combine with alkali at or near pH 4.8. Similarly, the form of the curve showing the reduction in the resistance of wool fibres to extension in media of varying pH, as compared with distilled water at pH 5.5, fails to reveal the presence of an excess of basic side chains over and above what are required to combine with the acid side chains. It was therefore concluded that the free acid and basic side chains of wool are equivalent and are combined with one another to form salt linkages between the peptide chains.

Confirmation of this view was obtained by studying the elastic properties of fully deaminated fibres in buffer solutions of varying pH.<sup>16</sup> Human



hair was used and the critical conditions for complete deamination were established in the following manner<sup>17</sup> After being calibrated by 30 per cent extension in distilled water, single fibres were immersed in 40 c cs of the van Slyke reagent for varying times at 22° C, the reagent being renewed every 24 hours After being washed in running water overnight, the fibres were then stretched a second time in distilled water at 22° C They were then immersed for several hours in N/10 hydrochloric acid before being stretched a third time in this medium at 22·2° C Data for the percentage reduction in the resistance of the fibres to extension in water, and in hydrochloric acid, after deamination are given in Table II, illustrated by Fig 3

Table II

Time of Deamination (hours)	Reduction in resistance to extension in water (%)	Reduction in resistance to extension in N/10 HCl (%)	Increase in resistance to extension in water after quinone treatment (%)
0	—	28.2	20.6, 18.6
4	17.6	28.9	8.9
8	16.9	30.2	11.1
22	25.5	33.2	6.9
35	28.3	32.7	8.0
48	32.0	31.2	5.7
65	33.2	32.3	4.7
125	30.2	37.7	4.5

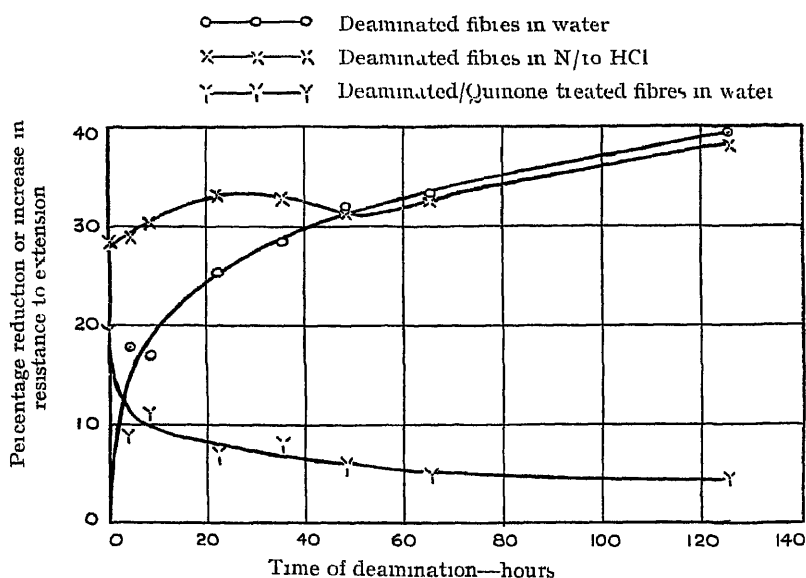


Fig 3

From 48 hours' deamination onwards, the behaviour of the fibres in water and in hydrochloric acid is essentially the same, indicating that complete deamination is realised in 48 hours under the above conditions

A series of fibres was therefore deaminated in two changes of the van Slyke reagent over a period of 48 hours at 22° C These fibres were then immersed in buffer solutions of varying pH values and, after a suitable time, stretched

30 per cent to determine the reduction in the resistance to extension in the buffer compared with distilled water at the same temperature (22.2° C). Corresponding experiments were carried out with untreated fibres, and the two sets of data are illustrated by Fig 4.

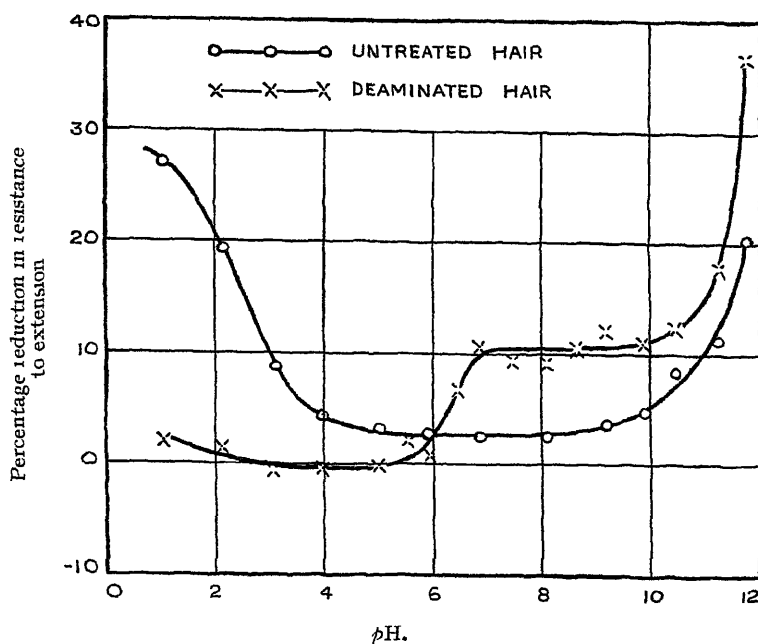


Fig 4

Unlike that of untreated fibres, the resistance of deaminated fibres to extension is sensibly independent of pH between pH 5 and 7, as would be expected if all the salt linkages were broken by complete deamination of the basic side chains. With the disappearance of the latter, however, a corresponding number of free carboxyl groups should become available for combination with alkali and, by analogy with the free carboxyl groups in gelatin, combination should begin at or about pH 5. That carboxyl groups are, in fact, liberated is evident from the sharp rise in the curve for deaminated fibres between pH 5 and 7. The reduced resistance to extension in this region is, of course, due to the swelling which follows combination of the carboxyl groups with alkali, and not to the breakdown of linkages. In consequence, no agreement can be expected between the reduction in the resistance of deaminated fibres to extension between pH 5 and 7, and that of untreated fibres between pH 5 and 7.

Arguments of this type, based on the elastic properties of animal fibres, have been disputed by Harris,<sup>18</sup> who claimed that the reduction in the resistance of untreated fibres to extension in acid is due not to breakdown of salt linkages, but to the swelling which follows combination of basic side chains with acid. In support of this view he showed that untreated fibres are *more* resistant to extension in N/10 hydrochloric acid solution saturated with salt than in water, despite the fact that the salt linkages must have been

broken in the former medium. The increased resistance to extension in HCl-NaCl was attributed to depression of swelling, and, conversely, the effect of HCl in reducing the resistance to extension in absence of salt was referred to increased swelling. Actually, however, the deduction is false because the comparison should be between fibres in water saturated with salt and in hydrochloric acid saturated with salt. Load-extension curves for the same fibre in water, in saturated salt solution and in N/10 hydrochloric acid saturated with salt, are shown in Fig. 5.

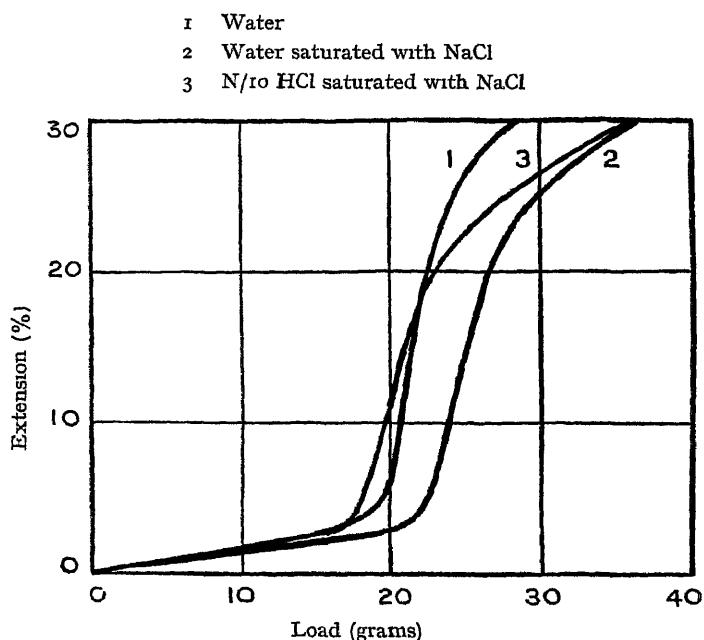
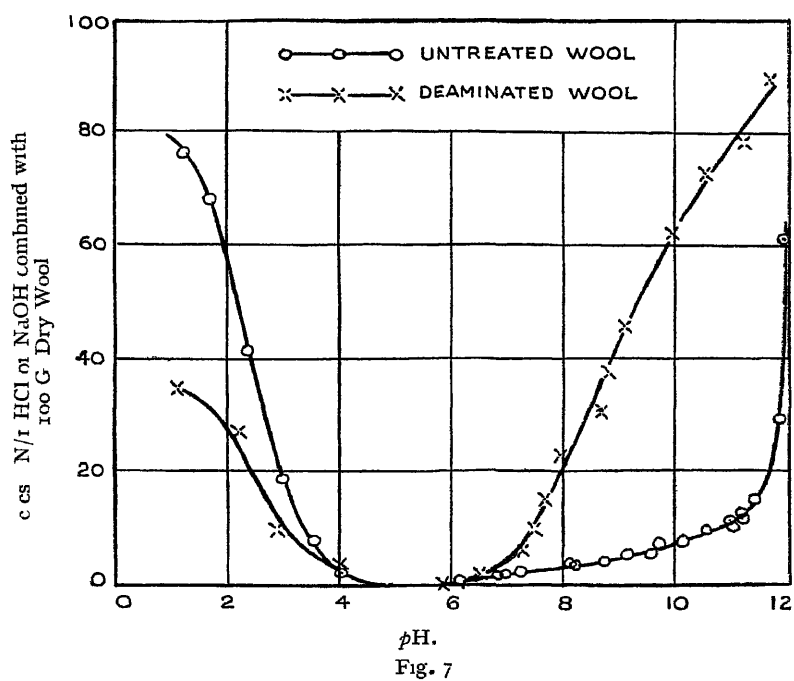
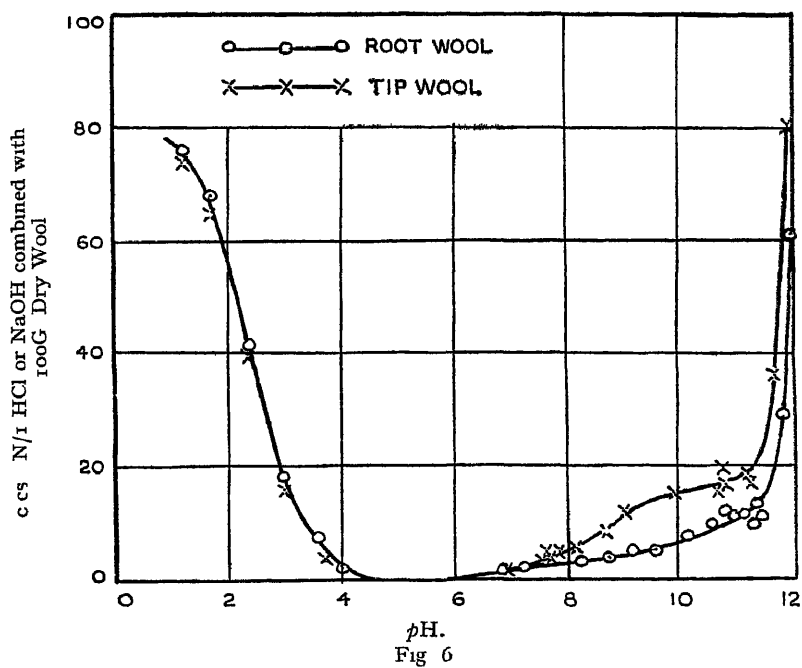


Fig. 5

The fibre is less resistant to extension in hydrochloric acid saturated with salt than in water saturated with salt, in agreement with the salt linkage hypothesis. In the case of strong acids like hydrochloric acid, the direct effect of swelling on the elastic properties of the fibre is small, although pronounced effects are produced by concentrated solutions of weak acids, as has been indicated elsewhere.

The argument in favour of the existence of salt linkages between the peptide chains of the wool fibre does not, however, rest solely or even mainly on the elastic properties of the fibre in different media. For example, the titration curve of wool<sup>19</sup> is closely related to the curve showing the reduction in the resistance of fibres to extension in media of varying *pH*. As shown in Fig. 6, both root and tip wools show no affinity for either acid or alkali over a well-defined range, and intact root wool combines with little alkali below *pH* 10.

Further, when wool is deaminated, the reduced affinity for acid at *pH* 1 is accompanied by a rise in the affinity for alkali at low *pH* values, as is shown by the titration curves of untreated and partially deaminated New Zealand Romney wools<sup>20</sup> (Fig. 7). The fact that the rise in the affinity for alkali



commences at a higher  $pH$  value (6.7) than in Fig 4 ( $pH$  5) is, of course, due to the use of unbuffered solutions in the determination of the titration curves. In the absence of salt, the difference between the internal  $pH$  of the fibre, and the measured external  $pH$  of the medium with which it is in equilibrium, is considerable.

Determinations of the heat of reaction of wool with acids have also given results in conformity with the salt linkage hypothesis.<sup>21</sup> In the case of hydrochloric acid, a value of 3.56 kcal per gram-molecule of combined acid was obtained, whereas a very much higher value was to be expected if the strongly basic side chains of lysine and arginine were free, i.e., uncombined with the acid side chains of aspartic and glutamic acids. As was indicated when the salt linkage hypothesis was first advanced,\* the combination of wool with acids takes place by back-titration of the carboxyl groups in salt linkages, and the low heat of reaction of wool with acids is in agreement with this view.

Finally, recent determinations of the amounts of aspartic and glutamic acids in wool,<sup>22</sup> which it has not yet been possible to publish in full, show that these acids are present in amounts sufficient to account for the arginine, lysine and histidine side chains and amide nitrogen. Cotswold wool was used and the data are given below.—

Acid	Amount isolated expressed as	
	Per cent on weight of dry wool	Mgm N/g of dry wool
Glutamic acid	15.27	14.54
Aspartic acid	7.27	7.65
	Total N =	22.19

The amide nitrogen content of wool was found to be 13.7 mgm/g, leaving dicarboxylic acid equivalent to 8.49 mgm N/g available for combination with the basic side chains. Taking Vickery and Block's determinations of the basic amino acids in wool,<sup>23</sup> the excess dicarboxylic acid required for combination according to the salt linkage theory is 8.55 mgm N/g. Vickery and Block's results are probably low, but even if the maximum combining capacity of wool for hydrochloric acid is taken as a measure of the basic amino acid content, the amount of dicarboxylic acid needed for combination is only 11.2 mgm N/g. In other words, 22.19 out of the maximum possible requirement of 24.9 mgm N/g have been isolated. This fact, taken in conjunction with earlier argument, seems to substantiate the view that the free acid and basic side chains of wool are equivalent and are combined with one another to form salt linkages between the peptide chains of the fibre.

Reference has already been made to the growing belief that the main peptide chains of proteins are built up from the amino acids according to some definite plan. In this connection, attention must here be drawn to the constancy of the acid-combining capacity of wool and related fibres. The types examined in this laboratory have ranged from Merino and New Zealand

\*This fact appears to have been overlooked by Steinhardt, Fugitt and Harris (*Amer. Dyestuff Rep.*, 1940, 29, 626.)

Romney wools, through the English wools—Cotswold, Leicester and South Devon—to human hair, and despite considerable variations in sulphur (cystine) content the maximum acid-combining capacity was found to be constant within very small limits. The same value of 80 c cs N/1 HCl per 100 g dry wool has been obtained by other observers in Germany, U S A, and elsewhere, and it seems clear that the acid-combining capacity of wool, no matter what its origin, is a constant. This, in turn, implies that the basic amino acid content of wool is constant, and, if the salt linkage hypothesis is correct, that the amount of free aspartic and glutamic acid is constant. The basic amino acids in wool—arginine, lysine and histidine—together with the equivalent amounts of aspartic and glutamic acid, represent a high proportion of the wool fibre (about 25 per cent by weight), and the constancy of this proportion must surely imply the existence of a determining mechanism in the synthesis of the fibre. This mechanism, besides controlling the total quantities of basic and dicarboxylic amino acids introduced, must also determine their relative positions in such a way that salt linkage formation can occur. An attempt is now being made to interpret the significance of this deduction.

(c) *The cystine linkage* Since cystine is a diamino-dicarboxylic acid, there is a fundamental probability that it forms linkages between the peptide chains as shown in Fig 1, and variations in the sulphur content of different wools are interpreted as being due simply to variations in the number of cystine linkages. The existence of covalent bonds between the peptide chains of wool must, of course, reduce its solubility, and it is not surprising, therefore, that von Weimarn<sup>24</sup> found keratin to be the most insoluble of a series of little soluble proteins. Conversely, disulphide bond breakdown should lead to increased solubility, and the alkaline reducing agents, such as sodium sulphide, dissolve wool readily on account of their ability to reduce cystine to cysteine. With sodium sulphide, complicated side reactions are possible, and in order to prove that cystine linkages are responsible for the insolubility of keratin, a simpler reagent is required. This was found in chlorine peroxide, which Schmidt has shown to attack tyrosine, tryptophane, histidine and cystine, although other amino acids and simple peptides are unaffected.<sup>25</sup> Cystine is oxidised to cysteic acid, and in view of the observation that simple peptides are unattacked, it seemed possible that the treatment of wool with an aqueous solution of chlorine peroxide would promote disulphide bond breakdown without main chain attack. The reaction was therefore investigated in conjunction with B Nilsen. Flocks were obtained from a scoured Southdown fabric by passing it through a cropping machine several times in succession with progressive lowering of the cutting blade. After being passed through a 30-mesh sieve to remove long fibre, the flocks were reduced to powder in a ball mill. At the end of this operation, the powder was passed through a 100-mesh sieve before being extracted with alcohol and ether. Mineral matter, derived mainly from the ball mill, was removed by stirring the powder with chloroform and centrifuging the suspension. The wool, which collected at the surface, was again washed with alcohol, followed by several changes of distilled water, before being allowed to dry in the air.

The chlorine peroxide solutions were prepared from potassium chlorate, oxalic acid and sulphuric acid, according to the method of Schmidt, and were freed from traces of chlorine by freezing. The chlorine peroxide hydrate

which separated was filtered off and re-dissolved in water. Solutions prepared in this way gave only a faint opalescence with silver nitrate, and were used under the following conditions. Powdered wool (30 g) was wetted out with 1 litre of distilled water, to which 2 per cent chlorine peroxide solution was added in an amount twice that necessary to oxidise the sulphur content (3.5 per cent) to sulphonic acid groups. The reaction mixture was stirred mechanically, samples being withdrawn at intervals to test for the presence of unoxidised sulphur. Two tests were employed, using suspensions from which excess chlorine peroxide was removed by means of sulphur dioxide, excess sulphur dioxide being afterwards expelled by boiling. In the first test, the suspension was made strongly alkaline with sodium hydroxide solution, lead acetate was added and the whole boiled for a few minutes. Blackening indicated the presence of unoxidised sulphur. In the second test, the suspension was boiled with sodium hydroxide alone and then tested for the presence of sulphhydryl groups with sodium nitroprusside. When oxidation was complete, the reaction product was filtered off, washed with distilled water for several hours, and then dried. As expected, the filtrate gave not the slightest reaction for sulphuric acid. The solubility of the reaction product in various media was then examined.

- (i) *Acids*. Complete solution was not realised. With excess of 5*N* hydrochloric acid, the amount dissolved in 46 hours at room temperature was found to be 26 per cent. Concentrated formic acid (98 per cent) caused intense swelling, the substance being converted into an almost homogeneous jelly, but without dissolution.
- (ii) *Alkalis*. With caustic alkalis in excess, the substance dissolved readily, but only 20 per cent could be recovered by acidifying the solution in 5*N* sodium hydroxide.
- (iii) *Alkaline metal oxide solutions*. The treated wool was only partially soluble in Schweizer's, Richardson's and Loewe's reagents.
- (iv) *Urea*. A concentrated solution of urea was ineffective, but molten urea dissolved the reaction product, apparently with partial decomposition.
- (v) *Neutral salts*. The product was readily soluble in Elsner's reagent (basic zinc chloride solution), and concentrated solutions of lithium iodide and lithium thiocyanate. Except in the case of lithium thiocyanate solution, which dissolves the treated wool at temperatures below 100° C, strong heating is essential.

In general, the treated wool is more resistant to dissolution than related protein fibres, but its solubility in lithium thiocyanate solution affords a further proof that the cystine linkages in untreated wool contribute very largely to its insolubility. Before discussing other evidence regarding the nature and location of the cystine linkage, reference must here be made to the fact that the treated wool is readily separated into three main fractions by alcoholic precipitation from lithium thiocyanate solution. Using the solution obtained by heating 2.5 g of the powdered, chlorine peroxide-treated wool on a steam bath with 30 g lithium thiocyanate and 5 cc water, addition of increasing quantities of alcohol gave increasing amounts of precipitate, as shown in Table III. The two main precipitates differ as regards their viscosity in sodium hydroxide solution, and the third, soluble fraction is presumably that which is extracted by 5*N* hydrochloric acid from

Table III

Alcohol added (c cs )	Precipitate (%)
25	22.2
75	2.1
225	52.3
975	8.2
1,975	1.0
2,975	—

the original, chlorine peroxide-treated wool. Whether the three fractions are related to the three phases<sup>5</sup> in animal fibres is as yet unknown, and caution must be exercised in interpreting the results because evidence was obtained of a slow general attack on the fibre structure. Although it is now possible to dissolve wool without serious attack on the main peptide chains, some considerable time must elapse before satisfactory synthetic fibres can be made from waste wool. Many problems remain to be solved, including that of discovering how to utilise sulphonic groups (cysteic acid side-chains) in cross-linkage formation.

Further evidence in favour of the view that the main peptide chains of wool are bridged by cystine linkages is afforded by the phenomenon of super-contraction. The folding of main peptide chains in accordance with the scheme shown in Fig 2 is regarded as being stabilised by cross-linkages between the chains. Should this be the case, further folding would occur when the cross-linkages are broken, and the fibre would contract to a length less than the original length (super-contraction). In support of the view that cystine forms cross-linkages between the peptide chains, it has been shown that reagents such as sodium sulphide, sodium bisulphite, potassium cyanide and silver sulphate, which are known to be capable of breaking the disulphide bond of cystine, bring about the super-contraction of wool fibres.<sup>26</sup> Similarly, chlorine peroxide-treated fibres were found to contract 58 per cent when boiled in *N*/10 hydrochloric acid for one hour, and the combined action of sunlight and air, which has been shown to be restricted to the cystine linkage, promotes the super-contraction of exposed fibres. In the case of bisulphite-treated fibres, however, Harrison has objected that the contraction takes place during drying and is caused by differential drying of the cuticle and its contents.<sup>27</sup> By carefully controlled drying at room temperature without tension, he claims to have reduced the super-contraction of bisulphite-treated fibres to 2 per cent. Actually, however, there is no substance in this criticism, because the bisulphite-treated fibres show a contraction of 8.9 per cent while still swollen in water.<sup>28</sup> Secondly, despite prolonged correspondence with Harrison, and repeated attempts by various observers to reproduce his experimental conditions, it has been found totally impossible to prevent the super-contraction of bisulphite-treated fibres during drying, if drying is carried out in complete absence of tension. Harrison's further difficulty, that the X-ray photograph of super-contracted fibres is the  $\beta$ -photograph of stretched fibres, has already been fully explained by Astbury and Woods.<sup>29</sup>

With many reagents, the degree of super-contraction is determined by two opposing reactions—disulphide bond breakdown and the formation of new linkages. Sodium sulphite, for example, is known to cause disulphide bond breakdown in the case of cystine, but wool fibres do not super-contract



in boiling solutions of this reagent. The anomaly is due to the fact that sodium sulphite is less reactive than sodium bisulphite with cystine linkages, and, as will be shown below, promotes the formation of new cross-linkages between the peptide chains. Such cross-linkages, which oppose super-contraction, are formed by the interaction of the products of hydrolysis of the cystine linkage and the basic side chains. When the latter are removed by deamination, wool fibres super-contract in boiling sodium sulphite solution. Similarly, deaminated fibres super-contract in boiling 2 per cent borax solution, which has no effect in promoting the contraction of untreated fibres. The failure of sodium sulphite and borax to bring about super-contraction in the case of untreated fibres may also be connected with their inability to cause marked breakdown of the salt linkages, which have a stabilising effect on the molecular structure of the fibre, but the chief cause is the scheme of opposing reactions outlined above. In a recent paper, Elod<sup>30</sup> has shown that the treatment of wool fibres with water at 80° C in presence of mercury fails to promote super-contraction, even in hot hydrochloric acid at  $pH_2$ , despite the removal of about 45 per cent of the total sulphur. The fibres were, however, heated with water for several days, and linkage rebuilding might well occur in the unstretched fibres. Secondly, mercury compounds have been shown to be singularly effective linkage-rebuilding agents, and any mercury-containing cross-linkages would oppose super-contraction. Such effects may well be present, but a repetition of Elod's experiments with human hair, showed that the mercury-treated fibres (22 days at 80° C), while incapable of contraction in boiling water, gave 42 per cent super-contraction in boiling 2 per cent borax solution. In all cases, therefore, disulphide bond breakdown promotes super-contraction, confirming the view that the main peptide chains of wool are bridged by cystine linkages as shown in Fig. 1.

#### Technical Significance of the Constitution of the Keratin Molecule

Following the general trend of recent research, the dyeing and finishing processes of the wool textile trade will now be discussed and interpreted in terms of the three main features of the keratin molecule, viz., main peptide chains, cystine linkages and salt linkages.

(a) *Milling* Some years ago it was shown that, for milling shrinkage to be possible, fibres must possess three main properties—a surface scale structure, ease of deformation and power of recovery from deformation.<sup>31</sup> During milling, the fibres migrate in much the same way as a worm crawls,<sup>32</sup> shrinkage being promoted by acids, which break down the salt linkages and facilitate fibre extension. At the same time, the power of recovery is left sensibly unchanged, and the tendency for mill rigs to develop is small. In alkaline media, on the other hand, fibre deformation is promoted and milling assisted by attack on both the salt and the sulphur linkages, but the power of recovery is reduced by disulphide bond attack, and this factor overwhelms the increasing ease of extension at  $pH$  values above 10 at ordinary temperatures. The existence of an optimum  $pH$  for milling in alkaline media is thus directly attributable to the properties of the cystine linkage. Similarly, the existence of an optimum temperature for milling with both soap and acid must be referred to the fact that the disulphide bonds of animal fibres are hydrolysed by water at high temperatures, especially when the fibres are strained.

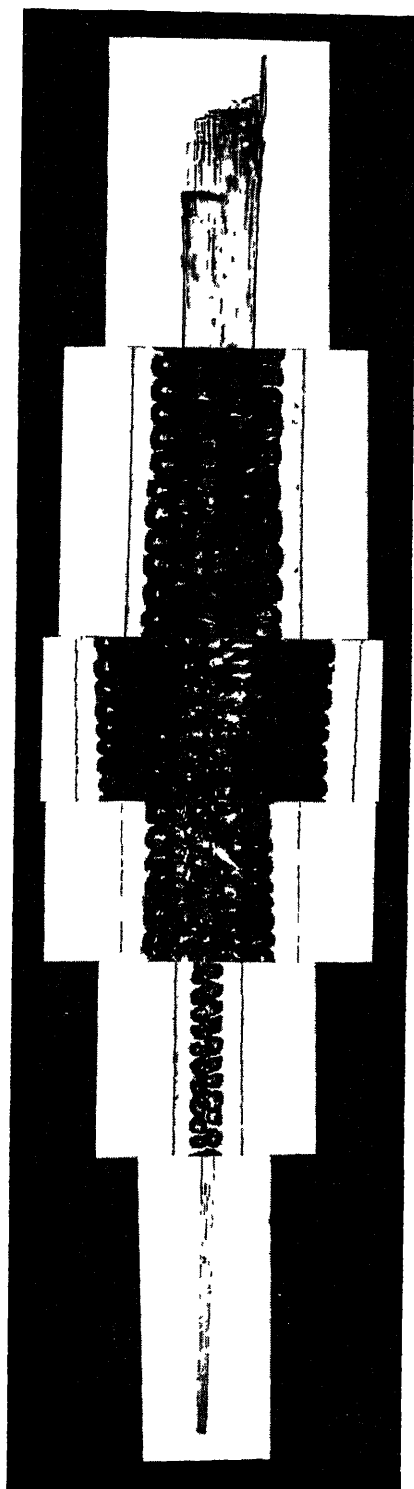
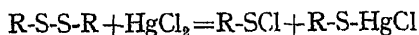


Fig. 8

(b) *Carrotting* Although disulphide bond breakdown, when severe, militates against milling, rabbit fibres are treated with agents such as mercuric nitrate in nitric acid, hydrogen peroxide, per-acids and per-salts, in order to increase their felting properties. All such agents have one property in common, their ability to promote disulphide bond breakdown. Mercuric chloride, for example, is known to react with the disulphide bonds of wool and hair in accordance with the following equation:—



Mercuric nitrate reacts in a similar manner, except that more severe disulphide bond breakdown is induced by the severe oxidising action of both the nitrate and the nitric acid in which it is dissolved. An explanation of the apparent anomaly that severe disulphide bond breakdown promotes felting in the case of fur fibres, and prevents felting in the case of wool fibres, was found



Fig 9

in terms of the peculiar contour of the rabbit and hare fibres. The work was carried out in conjunction with Dr N H Chamberlain and Dr E C Fairhead, and five photomicrographs, taken at intervals along the length of a single rabbit fibre, are shown together in Fig 8. Near the very fine tip of the fibre is a pronounced bulge which thins down towards the root end, which is coarser than the tip. During felting, the fibres tend to migrate towards the root end, but in the case of fibres possessing the peculiar shape of rabbit hairs, it is clear that migration will be impeded by the bulbous region towards the tip. Entanglements which can be penetrated by the root end will offer serious obstruction to the bulb, but if the latter is softened by severe disulphide bond breakdown, much freer migration and felting would be possible. In its tendency to migrate, the root end would stretch and thin

down the bulb, thus facilitating the migration of the fibre as a whole. Complete confirmation of this deduction is to be found in the fact that, in carotting practice, treatment with mercuric nitrate and nitric acid is restricted to the upper (tip) half of the fibres containing the bulbs. This effect is clearly revealed in Fig 9, which shows a section of a commercially carotted skin. The skin, with the fibres still attached, was immersed in  $H_2S$ -water and the deposit of mercuric sulphide is clearly restricted to the tips of the fibres. Further, if the rabbit fibres are cut from the skin, and then treated with a solution of mercuric nitrate in nitric acid, their felting properties are decidedly inferior to those in which attack is restricted to the tips. There can be no doubt, therefore, that the function of carotting agents is to soften or plasticise the bulbous regions on fur fibres, leaving the root ends intact. In the past, it has been supposed that carotting agents augment the felting power of fur fibres by accentuating their scaliness, but microscopic observation failed to reveal any such effect.

The behaviour of mixtures of wool and synthetic protein fibres is closely related to that of carotted fibres. In the latter case, one section of each fibre is normal and the other pliable, or even plastic; in the former case, normal wool fibres operate in a matrix of plastic fibres, fibre migration is promoted and shrinkage enhanced. An example of this kind of effect has been found in mixtures of wool and casein fibre,<sup>33</sup> and a second illustration is given below. Mixtures of wool and a second synthetic protein fibre were carded and spun to 15's YS woollen yarn with 10 turns/inch twist. The several yarns were then woven as weft on a cotton warp and milled with soap in a milling machine, the width shrinkage being measured at intervals. Typical results are given in Table IV.<sup>34</sup>

Table IV

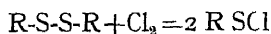
Composition of blend per cent by weight of		Percentage shrinkage in width after 50 minutes
Wool	Protein fibre	
100	—	13.3
75	25	17.6
50	50	20.0

As would be expected, the phenomenon is not restricted to protein fibres, but seems to be true of all fibres which, under milling conditions, become plastic. For milling to be possible, such fibres must, of course, be used in conjunction with fibres possessing a surface scale structure.

(c) *The Unshrinkable Finish* In terms of the nature of milling shrinkage, it should be possible to reduce the felting power of wool either by modifying the surface scale structure or by modifying its elastic properties. Examples of the manner in which modified elastic properties may reduce the felting power of wool have been found in the case of heavily dyed fibres and fibres treated with the tannic acid-tar-tar emetic resist.<sup>35</sup> In both cases, reduced felting is due to an increased resistance to deformation, and a reduced power of recovery, brought about by the impedance offered by the dye molecules or the resist to the unfolding and folding of the main peptide chains.

The more usual method of reducing the felting power of wool is by modifying the surface scale structure. In the Craven process,<sup>36</sup> the scale layer is masked by a film of aluminium or chromium hydroxide (or hydrated

compounds derived from basic aluminium and basic chromium sulphate liquors by membrane hydrolysis), and the reduced shrinkage of the treated wool affords one of the simplest proofs that a surface scale structure is essential if fibres are to undergo milling shrinkage. The commercial method of making wool unshrinkable is by treatment with an aqueous solution of chlorine or hypochlorous acid, when the layer of cortex immediately underlying the scales is attacked preferentially.<sup>37</sup> Some surface reaction may also occur, disulphide bond breakdown being brought about by the following primary reaction —



As a result, the attacked structure swells and gelatinises in acids and alkalis, especially the latter, with the result that milling shrinkage is prevented either by loss of scales, where there is underlying attack, or by surface slipperiness (masking of the scale layer) as in the case of the Craven process. In order to obtain more even treatment of wool than is possible in wet chlorination, chlorine is sometimes applied as a gas to wool of low water content.<sup>38</sup> When unswollen, the fibres are less accessible to the reagent, attack is restricted to the surface, and the danger of excessive damage is reduced.

As a corollary to the preceding discussion of chlorination processes, it is evident that any reagent which is capable of gelatinising the wool fibre should be capable of giving an unshrinkable finish, provided it is applied under such conditions that its attack is restricted to the surface of the fibres.<sup>39</sup> Gelatinisation may be brought about by the fission of either disulphide bonds or peptide linkages, or both, and there seems now to be no limit to the number of ways in which wool fabrics may be made unshrinkable. As regards disulphide bond attack, the first constructive attempt to use the above principles was made in 1936 when chlorine peroxide, which gelatinises wool by converting cystine linkages into cysteic acid side-chains, was applied to air-dry wool from solution in carbon tetrachloride.<sup>40</sup> Attack was restricted to the surface of the fibres because the large chlorine peroxide molecules, being dissolved in a non-swelling solvent, found it difficult to penetrate the relatively unswollen, air-dry wool. The following example will suffice to indicate how little chlorine peroxide is required to reduce the felting power of wool under the above conditions.<sup>41</sup> A rectangle of a South-down fabric (30 in. × 36 in.) was conditioned in a room at 65 per cent relative humidity and 22.2° C for several days before being weighed (250.6 g) and immersed in 7 litres of a 0.082 per cent (wt/vol) solution of chlorine peroxide in carbon tetrachloride for eight hours. The fabric was then treated with 2 per cent sodium bisulphite solution for 45 minutes and washed in running water overnight. Both the treated fabric, and a second rectangle of the untreated fabric, which had been wetted-out with water, were freed from excess water by centrifuging and then milled together with soap in the fulling stocks. The area of each fabric was measured at intervals, and data for the percentage reduction in area are given in Table V.

Similarly, Hall's discovery<sup>42</sup> that a solution of sulphuryl chloride in white spirit, when applied to wool of low water content (12–14 per cent regain), is capable of giving a high degree of unshrinkability with little fibre damage, has since been shown to be due to the action of sulphuryl chloride in causing disulphide bond breakdown.<sup>43</sup> Once again, surface attack is realised by applying the reagent from a non-swelling solvent to the relatively unswollen,

air-dry fibres Perhaps the most striking confirmation of the general theory of unshrinkability is, however, to be found in the fact that caustic alkalis,<sup>44</sup> such as sodium hydroxide, which hydrolyse disulphide bonds, and alkaline reducing agents, such as sodium sulphide,<sup>45</sup> which cause disulphide bond breakdown by hydrolysis and reduction, have been found to make wool unshrinkable when applied to the air-dry material from non-swelling solvents so as to restrict attack to the surface of the fibres Finally, a combined attack on disulphide bonds and peptide linkages forms the basis of a recent process in which wool is treated with an enzyme, such as trypsin or papain, in presence of sodium sulphide or sodium bisulphite at elevated temperatures<sup>46</sup> By causing disulphide bond breakdown, the reducing agent facilitates hydrolysis of the peptide linkages by the enzyme, which has such a high molecular weight that its action is restricted to the surface of the fibres

Table V

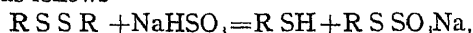
Time of milling (hours)	Percentage reduction in area of	
	Untreated fabric	Chlorine peroxide- treated fabric
2	6.9	3.9
4	11.1	7.2
6	17.2	6.5
8	21.6	6.5
10	26.0	8.8½

(d) *Dyeing* In the preceding section, there has been frequent reference to the inaccessibility of relatively unswollen, air-dry fibres to the molecules of chlorine peroxide, sulphuryl chloride and other simple compounds dissolved in non-swelling solvents Even when the fibres are swollen in water or dilute solutions of inorganic acids, the crystalline phase (micellar structure) is still difficult of access because swelling is restricted by the cross-linkages between the peptide chains For example, Astbury and Dawson have shown that, when wool is dyed with such a simple dye as Orange II from a boiling, dilute sulphuric acid dyebath, the dye does not gain access to the interior of the micelles<sup>47</sup> Similarly, as regards the fibre as a whole, it has been shown recently that compounds such as anthraquinone, anthraquinone-2-sulphonic acid and phenanthraquinone, unlike benzoquinone and naphthaquinone, are unable to form new linkages between the peptide chains by reaction with basic side-chains, presumably because the molecules are too large to gain access to the fine structure of the fibre<sup>48</sup> In dyeing, therefore, it seems clear that the smaller inorganic anions, which penetrate the micelles, are displaced from combination by the accumulation of coloured anions on the outer surfaces of the micelles, the process being akin to the mutual precipitation of oppositely charged colloids Surface adsorption of this type, and the orientation of the dye anions at the interface, will promote the formation of colloidal aggregates within the fibre In effect, adsorption on the surface of the micelles promotes aggregation by lowering the "temperature" of the coloured anions, and it is now clear why there is such a close connection between the sensitivity of a dye to precipitation by acid and salt—its colloid character—at ordinary temperatures, and its tendency to give uneven dyeings in the boiling acid dyebath, even though the dye molecules are not aggregated in the boiling dyebath itself<sup>50</sup> Similarly, there is now no difficulty

in understanding why a dye molecule is able to exert its full valency, in accordance with the number of sulphonic groups it contains, despite the fact that simple chemical combination with the correct number of basic side chains would be impossible on stereochemical grounds even if micellar penetration were not excluded.<sup>49</sup> The significance of these observations in relation to the general theory of dyeing, and the work of Valkó<sup>50</sup> and Porai-Koschitz,<sup>51</sup> will receive further consideration elsewhere.

In terms of the above theory, it is obvious that there are two ways in which wool may be resisted against acid dyes—either by eliminating its basic properties, or by altering the sign of charge of the micelles in an acid bath. In practice both appear to be essential. For example, the resist faults which are encountered in carbonising are due not simply to a reduced basicity when the basic side chains are converted into sulphamic acid side-chains<sup>52</sup>— $RNH\cdot SO_3H$ —but to the effect of these acid groups in reducing the effective positive charge developed by the micelles in an acid dyebath. Evidence has been obtained recently that the sulphonation of tyrosine side-chains, in accordance with an earlier suggestion, contributes to the resist given by sulphuric acid treatment.<sup>53</sup> Similarly, it has been shown that resist effects are difficult to obtain by simple acetylation, which merely reduces the basicity of wool, whereas acetylation in presence of sulphuric acid gives greatly improved results.<sup>54</sup> More recently, the argument has been carried to its logical conclusion in a process which introduces an acid group for every basic group eliminated, without significant damage to the wool. The resist is good, and full details will shortly be released.

(e) *Creping* There are two general methods of developing wool crepes. The first, which is rarely used, is based on the ability of wool fibres to super-contract when they are boiled or steamed in presence of reagents which cause severe disulphide bond breakdown. Among suitable reagents are sodium bisulphite<sup>55</sup> and calcium thiocyanate<sup>56</sup>. The former reacts with cystine linkages as follows —



and the latter, on being steamed, is converted into calcium hydrosulphide, which reduces the disulphide bonds to cysteine side-chains under alkaline conditions. Unfortunately for the success of these processes, disulphide bond breakdown is inseparable from fibre damage, and chemical methods of developing wool crepes have seen little or no practical application. It seems likely, however, that their period of desuetude has been brought to an end by the discovery of methods of repairing the fibre damage caused by reagents such as sodium bisulphite and alkaline reducing agents. These methods receive discussion later in the paper, and their application to the damaged fibres of chemically-developed wool crepes will permit important developments in the finishing of wool textile materials.

The second, and more usual, method of producing wool crepes is based on the use of hard-twisted yarns. When a fabric containing such yarns is wetted out, the torsional forces are freed to cause distortion of the weakened structure. The conditions of development must, however, be so chosen that the torsional forces are able to cause distortion before they disappear by relaxation processes within the fibres. Boiling water, for example, is an unsuitable medium for the development of wool crepes, because it promotes severe disulphide bond breakdown in deformed fibres, and thereby causes such rapid decay of stress that full distortion of the structure cannot be

realised. Conversely, ice-cold water is unsuitable because, although the rate of decay of stress is small, the fabric offers too great a resistance to deformation. As shown in Fig 10, where the percentage shrinkage in area of a crepe fabric is shown as a function of the temperature of the distilled water in which it was immersed, with mild agitation, for two hours, the optimum temperature for developing wool crepes appears to be about  $42^{\circ}\text{C}$  at pH 5-6.<sup>57</sup> This temperature is one which is critical in many processes and seems to be associated with the onset of disulphide bond hydrolysis.<sup>58</sup> Since the rate of decay of stress in deformed fibres is greatest in alkaline and least in acid media,<sup>59</sup> acid conditions should be particularly suitable for creping processes. This is in fact the case, and it has been found that successful crepes can be obtained at temperatures as high as  $80^{\circ}\text{C}$  in strongly acid media, although there is no advantage in raising the temperature above  $42^{\circ}\text{C}$ .

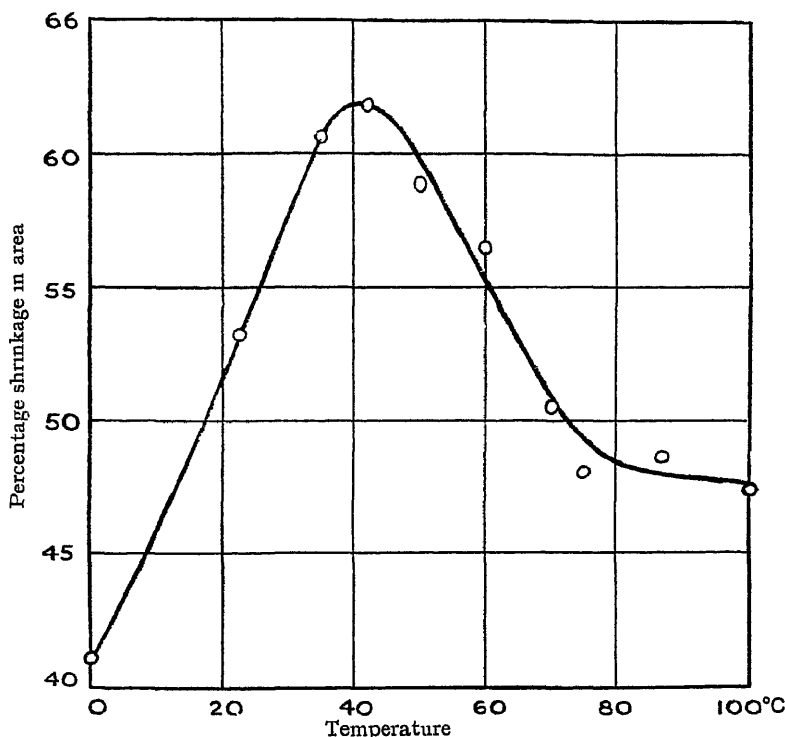
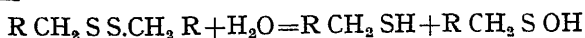


Fig 10

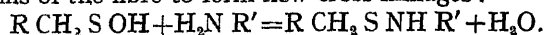
(f) *Setting—crabbing and blowing*<sup>60</sup> When wool fibres are stretched, the long, folded peptide chains uncoil against the resistance of cross-linkages, into which stress is thrown. Unlike salt linkages, cystine linkages are capable of supporting stress without immediate rupture in water at low temperatures, and this stress promotes the rapid return of the fibres to their original length on release in water. When stretched fibres are steamed for a short time, however, internal stress is rapidly dissipated by disulphide bond hydrolysis —



In this state, the fibres are capable of contracting to a length less than the original length, because disulphide bond breakdown removes the main

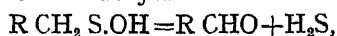


restriction to folding of the peptide chains beyond the state shown in Fig 2, but the contractile force is extremely small. If steaming is prolonged, the sulphenic acid, formed in accordance with the above equation, reacts with the basic side chains of the fibre to form new cross-linkages:—

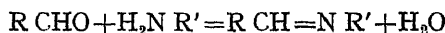


Besides restoring strength to the fibre, these new linkages, being formed in the relaxed structure, prevent contraction when the fibre is released in cold water. Although some contraction is possible, the fibre fails to return to its original length in steam or boiling water, and the magnitude of this true permanent set increases with increasing time of steaming of the stretched fibre. Thus the setting of strained animal fibres in steam may be expressed very simply in terms of two successive chemical reactions within the fibres.

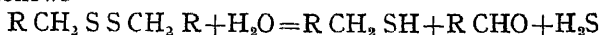
Since disulphide bond hydrolysis is essential for set, it would be expected that boiling dilute solutions of alkalis would give more rapid setting of strained fibres than steam or boiling water. In agreement with this deduction, it has been shown that the optimum pH for setting is pH 9.2 in the case of simple acids and alkalis,<sup>60</sup> but the reactions within the fibres are more complicated than in steam or boiling water. The sulphenic acid is unstable in alkalis and decomposes to give an aldehyde<sup>61</sup> —



and the aldehyde reacts with basic side chains to form a new type of cross-linkage<sup>62</sup> —

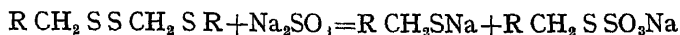


In part, the reaction proceeds in the same way as in steam or boiling water, giving  $RCH_2SNH R'$  cross-linkages, but  $RCH=N R'$  cross-linkages are formed as well. That the latter type of cross-linkage is not the more important in setting processes seems to be established by the fact that the ability of animal fibres to acquire a permanent set in steam is reduced by exposure to light and air<sup>60</sup>. Under the latter conditions, the disulphide bonds are hydrolysed and the sulphenic acid decomposes to give aldehyde groups as follows<sup>63</sup> —



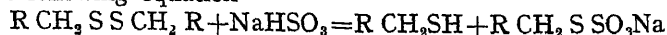
Despite the fact that the first stage of setting is accomplished prior to the setting process proper, setting properties are impaired by exposure to light and air.

Similarly, sodium sulphite is a useful assistant in setting processes on account of its ability to promote disulphide bond breakdown in strained fibres —



The thiosulphate then reacts either directly, or as a sulphenic acid after hydrolysis, with basic side chains to form the  $-SNH-$  type of cross-linkage. Since sodium sulphite solution is alkaline, however, it behaves, in part, as a simple alkali and some  $-CH=N-$  cross-linkages are also formed, though not to the same extent as in a 2 per cent borax solution at pH 9.2.

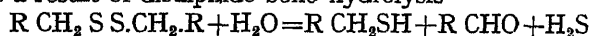
Even more effective than alkalis or sodium sulphite is sodium bisulphite in setting animal fibres. Disulphide bond breakdown occurs in accordance with the following equation —



and set is due to the formation of  $-SNH-$  cross-linkages, supported probably by re-formed disulphide bonds. Since the bisulphite solution is acid (pH 4),

any sulphenic acid formed by hydrolysis of the thiosulphate is much more stable, and  $-\text{CH}=\text{N}-$  linkages are not formed

In agreement with the chemical mechanism of permanent set outlined above, it has been shown that pre-treatment of animal fibres with sodium hydroxide solution, and removal of sulphur with baryta water, both impair the ability to acquire a permanent set<sup>64</sup> More recently, however, Elod, Nowotny and Zahn<sup>30</sup>, making use of a reaction discovered in this laboratory, claim to have shown that disulphide bond breakdown is neither an essential preliminary to the setting of strained animal fibres, nor a necessary cause of super-contraction Wool fibres were heated with water in presence of mercury at 80° C, hydrogen sulphide being liberated and mercuric sulphide formed as a result of disulphide bond hydrolysis —



Although 45 per cent of the total sulphur was removed in 19 days, suggesting that 90 per cent of the disulphide bonds were hydrolysed, the fibres showed no tendency to contract in either boiling water or boiling hydrochloric acid at pH 2, and their setting power (in an unspecified medium) was unimpaired

As already indicated (p 96), the failure of the mercury-treated fibres to super-contract might be due to the occurrence of setting reactions in the unstretched fibres during prolonged heating in water at 80° C, especially as mercury compounds have been shown to be specially effective in promoting cross-linkage formation Elod himself refers to the tanning action of the mercuric sulphide, but if cross-linkage formation is invoked to explain the absence of super-contraction, the difficulty of accounting for unimpaired setting properties becomes more acute. There can be no doubt, therefore, that if Elod's observations are correct, the present theory of the chemical mechanism of permanent set is invalidated In consequence, the properties of mercury-treated fibres were re-examined

Because of its higher sulphur content, human hair was used in preference to wool so that the course of disulphide bond attack could be followed more readily After purification by extraction with alcohol, ether and distilled water, the fibres were heated for several days at 80° C with distilled water and purified mercury in a quartz tube Fibres were removed at intervals and their setting power determined in the usual way, each fibre being stretched 40 per cent in cold water and then set by immersion in boiling 2 per cent. borax solution for 30 minutes The set retained by the fibre after various times of release in boiling water was determined by measuring its air-dry length, drying being allowed to proceed in absence of tension Typical data are given in Table VI, from which it is clear that the ability of animal fibres to acquire a permanent set decreases with increasing time of heating with water and mercury at 80° C

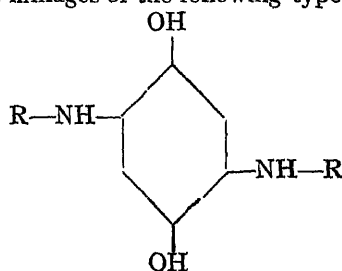
Table VI

Time of treatment with water and mercury at 80° C	Percentage set after release in boiling water for				
	0'	2'	15'	30'	60'
Untreated	40.2	24.0	22.3	22.5	22.2
6 days 2 hours 15 minutes	40.4	19.0	17.6	17.4	17.1
8 " 23 " 6 "	40.2	15.9	15.2	14.9	14.4
13 " 3 " 50 " "	40.3	12.9	12.2	12.0	11.5
22 " 2 " 30 " "	40.3	2.9	1.6	1.1	0.5

Elöd's observations, therefore, appear to be incorrect, and the present conception of the chemical mechanism of permanent set remains valid.

(g) *Prevention and Repair of Damage.* During processing, wool is exposed to the action of acids and alkalis, as well as acid and alkaline oxidising and reducing agents, and it is inevitable that some degree of damage shall result. Its extent can, of course, be minimised by careful control of conditions, except in cases where damage is essential to the effect sought, as in the chemical development of wool crepes. Besides permitting improved products to be marketed, the discovery of effective methods of repairing damage to wool fibres would enlarge the range of possible finishing processes by bringing into service a number of reactions, which are at present excluded because of the damage they entail. It is not surprising, therefore, that much attention has been devoted recently to the synthesis of new cross-linkages between the peptide chains of animal fibres.

One of the earliest methods of increasing the strength of intact fibres consisted in treating them with an aqueous solution of benzoquinone.<sup>65</sup> The effect of boiling untreated and de-aminated fibres for one hour with a 2 per cent solution of benzoquinone in 2 per cent alcohol solution is illustrated by the data of Table II. Untreated fibres are strengthened very considerably, and the strengthening effect decreases with increasing degree of de-amination, indicating that the main reaction is with basic side chains. In all probability, cross-linkages of the following type are formed.—



but other reactions must occur, since some strengthening is obtained with fully de-aminated fibres. Similarly, at pH 6-7, formaldehyde is able to bridge basic side chains by the formation of  $\text{R NH CH}_2\text{NH R}$  cross-linkages.<sup>66</sup> In this case also, other reactions take place, but the strengthening effect of formaldehyde is less than that of quinone.

The first constructive attempts to repair fibre damage were made in connection with the development of low-temperature setting processes.<sup>69</sup> As has already been indicated, setting processes are based on two consecutive reactions in strained fibres—disulphide bond breakdown, followed by linkage rebuilding in the relaxed structure. Disulphide bond breakdown is brought about very readily at low temperatures by sodium bisulphite, especially in aqueous-alcoholic solution, and alkaline reducing agents. In the former case, the products of reaction are  $\text{R CH}_2\text{SH}$  and  $\text{R CH}_2\text{S SO}_3\text{Na}$  side chains (p 102), which undergo re-arrangement as the structure relaxes. Nevertheless, many mercapto and thiosulphate side-chains are within range of one another in the relaxed structure, and can be made to re-unite with formation of disulphide bonds— $\text{R CH}_2\text{S S CH}_2\text{R}$ —by the simple expedient of making the fibre alkaline with ammonia.<sup>67</sup> Supplementary bond rebuilding can be obtained by treating the fibre with an oxidising agent, such as potassium persulphate or hydrogen peroxide, when neighbouring mercapto side-chains

are oxidised to form disulphide bonds. In practice, the two treatments can be combined,<sup>68</sup> and the process, besides being a useful second-stage treatment in low temperature setting processes, is valuable in repairing the damage sustained by animal fibres in creping with sodium bisulphite, or in stripping dyed materials with sodium hydrosulphite. Similarly, when disulphide bond breakdown has been brought about by means of alkaline reducing agents —



the mercapto side-chains can be re-united by treatment with alkaline oxidising agents, preferably in presence of a swelling depressor, to re-form disulphide bonds.

Damage caused by disulphide bond breakdown can also be repaired by treating the fibres with metal salts.<sup>69</sup> Sodium aluminate is singularly effective with bisulphite-treated fibres,<sup>68</sup> in part, no doubt, because of its alkalinity. Among the simpler salts, mercuric acetate is the best,  $\text{R CH}_2\text{S Hg S CH}_2\text{R}$  and other cross-linkages being formed. Its effectiveness is not restricted to fibres damaged by acid or alkaline reducing agents: peroxide-bleached fibres have their strength restored by simple immersion in a 0.1M solution of mercuric acetate in 0.1N acetic acid. Although mercuric acetate is only of theoretical interest in connection with the repair of damage, other metal salts have already found commercial use. For example, the faulty dyeing of exposed wool, due to the action of light and air in causing disulphide bond breakdown, can be prevented by pre-treating the fibres with a solution of basic chromium acetate in dilute acetic acid.<sup>70</sup> As has already been indicated, each broken disulphide bond gives rise to a cysteine side-chain, but the distance apart of neighbouring cysteine side-chains in the damaged fibre is so great that they are incapable of being converted into disulphide bonds by oxidation. The basic chromium acetate, on the other hand, is polymerised, and the acetate radicals attached to the various chromium atoms in the chain can be displaced by single cysteine side-chains as they are encountered. Owing to the formation of metal-containing linkages in the damaged fibres, their swelling in water and dilute sulphuric acid is reduced to normal. For this reason, and because reducing mercapto groups are eliminated by cross-linkage formation, the dyeing properties of exposed wool, after treatment with basic chromium acetate, are similar to, if not identical with, those of untreated wool. The success which has attended this attempt to make use of linkage-rebuilding processes in repairing a particular type of fibre damage may be taken as significant of the developments which are to be expected in the finishing of wool textile materials.

Throughout this paper, the importance of recent advances in the chemistry of animal fibres has been illustrated by reference to finishing processes. Other sections of the industry are, of course, capable of equally precise treatment, and there can be no doubt that the Textile Institute is correct in insisting that the general and technical education of the future industrialist shall be essentially scientific in character.

#### REFERENCES

- <sup>1</sup> Barritt *J. Soc. Chem. Ind.*, 1928, 47, 697
- <sup>2</sup> Barritt and King *J. Text. Inst.*, 1926, 17, 1386
- <sup>3</sup> Bonsma *J. Text. Inst.*, 1931, 22, 1305
- <sup>4</sup> Speakman *J. Soc. Dyers and Col.*, Jubilee Number, 1934, p. 36
- <sup>5</sup> Astbury and Street *Phil. Trans. Roy. Soc. A*, 1931, 230, 75; Astbury and Woods, *loc. cit.*, 1933, 232, 333
- <sup>6</sup> Speakman and Hirst, *Trans. Faraday Soc.*, 1933, 29, 148; Speakman, *J. Soc. Dyers and Col.*, Jubilee Number, 1934, p. 34
- <sup>7</sup> Aberhalden and Fodor *Bei.*, 1916, 49, 561

- <sup>8</sup> Bergmann and Niemann *J Biol Chem*, 1936, 115, 77, 1937, 118, 301
- <sup>9</sup> Astbury and Bell *Nature*, 1941, 147, 696
- <sup>10</sup> Stakheyewa-Kaverznewa and Gavrilow *Bull Soc Chim (Mémoires)*, 1937, 4, 647;  
Speakman and McMahon, *Nature*, 1938, 141, 118
- <sup>11</sup> Neuberger *Proc Roy Soc., A*, 1939, 170, 64
- <sup>12</sup> Neurath *J Phys Chem*, 1940, 44, 296
- <sup>13</sup> Pauling and Niemann *J Amer Chem Soc*, 1939, 61, 1860
- <sup>14</sup> Speakman and Hirst *Nature*, 1931, 127, 665, *Trans Faraday Soc*, 1933, 29, 148.
- <sup>15</sup> Atkin and Douglas *J Soc Leather Trades' Chemists*, 1924, 8, 359
- <sup>16</sup> Speakman and Stott *Nature*, 1938, 141, 414
- <sup>17</sup> Speakman and Stoves In the press
- <sup>18</sup> Sookne and Harris *J Research Nat Bur Stand*, 1937, 19, 535
- <sup>19</sup> Speakman and Stott *Trans Faraday Soc*, 1934, 30, 539, 1935, 31, 1425,  
Speakman and McMahon, *loc cit*, 1937, 33, 844
- <sup>20</sup> Whewell and Speakman Unpublished investigation
- <sup>21</sup> Speakman and Stott *Trans Faraday Soc*, 1938, 34, 1203
- <sup>22</sup> Speakman and Townend *Nature*, 1937, 139, 411
- <sup>23</sup> Vickery and Block *J Biol Chem*, 1930, 86, 107
- <sup>24</sup> Von Weimarn *Koll Zeit*, 1926, 46, 120
- <sup>25</sup> Schmidt and Braunsdorf *Ber*, 1922, 55, 1529
- <sup>26</sup> Speakman *J Soc Dyers and Col*, 1936, 52, 335
- <sup>27</sup> Harrison *J Text Inst*, 1937, 28, P110, *Chem and Ind*, 1937, 56, 731
- <sup>28</sup> Speakman, Stoves and Bradbury *J Soc Dyers and Col*, 1941, 57, 73
- <sup>29</sup> Astbury and Woods *J Text Inst*, 1937, 28, P394
- <sup>30</sup> Elod, Nowotny and Zahn *Koll Zeit*, 1940, 93, 50
- <sup>31</sup> Speakman, Stott and Chang *J Text Inst*, 1933, 24, T273
- <sup>32</sup> Arnold *Leipziger Monats fur Textilind*, 1929, 44, 463, 507, 540
- <sup>33</sup> Diamond and Wormell *J Text Inst*, 1939, 30, P224
- <sup>34</sup> M C Liu Unpublished investigation
- <sup>35</sup> Liu, Speakman and King *J Soc Dyers and Col*, 1939, 55, 183
- <sup>36</sup> Craven British Patent No 290,805
- <sup>37</sup> Speakman and Goodings *J. Text Inst*, 1926, 17, T607
- <sup>38</sup> Wool Industries Research Association King and Galley British Patent  
No 417,719
- <sup>39</sup> Speakman, Nilssen and Elliott. *Nature*, 1938, 142, 1035
- <sup>40</sup> Nilssen Ph D Thesis, Leeds University, 1937.
- <sup>41</sup> Lal B Sc Thesis, Leeds University, 1937
- <sup>42</sup> Hall, Hicking and Pentecost British Patent No 464,503
- <sup>43</sup> Speakman, Nilssen and Elliott, *loc cit* Elliott and Speakman, *J Chem Soc*,  
1940, 641
- <sup>44</sup> Freney and Lipson Commonwealth of Australia Coun Sci Ind Res, Pamphlet  
No 94, 1940
- <sup>45</sup> Speakman and Farrington Patent Application, 1940
- <sup>46</sup> Phillips and Middlebrook British Patent No 513,919
- <sup>47</sup> Astbury and Dawson *J Soc Dyers and Col*, 1938, 54, 6
- <sup>48</sup> Speakman and Stoves. Unpublished investigation
- <sup>49</sup> Speakman and Clegg *J Soc Dyers and Col*, 1934, 50, 364
- <sup>50</sup> Valkó *J Soc Dyers and Col*, 1939, 55, 173
- <sup>51</sup> Porai-Koschitz, *loc cit*, 1936, 52, 19
- <sup>52</sup> Harris, Mease and Rutherford *J Research Nat Bur Stand*, 1937, 18, 343
- <sup>53</sup> M S Gaefer Unpublished investigation
- <sup>54</sup> Elliott and Speakman Unpublished investigation
- <sup>55</sup> Elsaesser G P 233-210
- <sup>56</sup> Justin-Mueller *Rev Gén Mat Col*, 1937, 41, 419
- <sup>57</sup> B Strmac Diploma Thesis, Leeds University, 1937
- <sup>58</sup> Speakman *J Text Inst*, 1936, 27, P231
- <sup>59</sup> Speakman and Shah *J Soc Dyers and Col*, 1941, 57, 108
- <sup>60</sup> Speakman *J Soc Dyers and Col*, 1936, 52, 335
- <sup>61</sup> Schoberl *Annalen*, 1933, 507, 111, *Collegium*, 1936, 412
- <sup>62</sup> Crowder and Harns *J Research Nat Bur Stand*, 1936, 16, 475
- <sup>63</sup> Phillips *Nature*, 1936, 138, 121 Speakman, *loc cit*, 1936, 138, 327. Speakman  
and Stoves *J Soc Dyers and Col*, 1937, 53, 236
- <sup>64</sup> Speakman and McMahon *Trans Faraday Soc*, 1937, 33, 844, Race, Rowe,  
Speakman and Vickerstaff *J Soc Dyers and Col*, 1938, 54, 141
- <sup>65</sup> Speakman and Whewell, *loc cit*, 1936, 52, 380
- <sup>66</sup> Meunier *J Soc Dyers and Col*, 1911, 27, 214
- <sup>67</sup> P L D Peill. Unpublished investigation
- <sup>68</sup> Footner and Smiles *J Chem Soc*, 1925, 127, 2887, Speakman, British Patent  
No 453,700, Speakman, Stoves and Bradbury, *J. Soc Dyers and Col*, 1941,  
57, 73
- <sup>69</sup> Speakman, Stoves and Bradbury, *loc cit*, 1941, 57, 80.
- <sup>70</sup> Speakman, *loc. cit*, 1936, 52, 423
- <sup>71</sup> Race, Rowe and Speakman, *loc cit*, 1938, 54, 159.

## 9—THE PROGRESSIVE OXIDATION OF COTTON CELLULOSE BY PERIODIC ACID AND METAPERIODATE OVER A WIDE RANGE OF OXYGEN CONSUMPTION

By G. F. DAVIDSON

(British Cotton Industry Research Association)

(Copyright by the Textile Institute)

### INTRODUCTION

Periodic acid is the only oxidizing agent whose primary reaction with cellulose is known with any certainty<sup>1, 2</sup>, and this fact gives the oxycelluloses prepared by its action a special importance in the study of chemically modified cellulose. The properties of the oxycelluloses formed in the very early stages of the oxidation of cotton cellulose by periodic acid and metaperiodate have already been described,<sup>3</sup> and the present paper records the results of an investigation of a much wider range of attack by these oxidants. Whereas the oxycelluloses previously examined corresponded for the most part to oxygen consumptions not greater than one atom to every hundred glucose units, the highest oxygen consumption in the present investigation exceeds one atom per glucose unit. The paper is largely concerned with the properties of the oxycelluloses resulting from the action of periodic acid and metaperiodate on cotton, but deals also with the identification and determination of certain other products of the oxidation.

### DESCRIPTION OF RESULTS

#### Copper Number, Methylene Blue Absorption and Fluidity of Oxycelluloses

It has been previously shown<sup>1</sup> that in the very early stages of the oxidation of cotton cellulose by periodic acid and metaperiodate increasing oxygen consumption produces a progressive increase of copper number and fluidity in cuprammonium solution, whilst the Methylene Blue absorption remains practically unchanged. Fig. 1 illustrates the variation of these properties with the oxygen consumption over a much wider range. It shows that although the oxycelluloses display very high reducing power, the copper number rising to a value 40 per cent. of that of glucose when the consumption of oxygen is one atom per glucose unit, the increase of copper number for a given oxygen consumption is considerably less in the later stages of oxidation than corresponds with the linear relation previously found to hold in the early stages<sup>3</sup>. The initial steep rise of the fluidity to a value of 55 at an oxygen consumption of 0.1 atom per glucose unit is followed by a much slower increase towards the limit of 72 set by the fluidity of the solvent. As the degree of oxidation increases the Methylene Blue absorption first decreases very slightly and then increases, but even at an oxygen consumption of one atom per glucose unit the absorption is no greater than that of a typical acidic oxycellulose resulting from the consumption of one thirtieth of this proportion of oxygen<sup>4</sup>. The variation of fluidity and copper number with oxygen consumption is substantially the same whether oxidation is by periodic acid or metaperiodate, but in the later stages of oxidation a periodic

acid oxycellulose displays a slightly greater affinity for Methylene Blue than the metaperiodate oxycellulose resulting from an equal consumption of oxygen

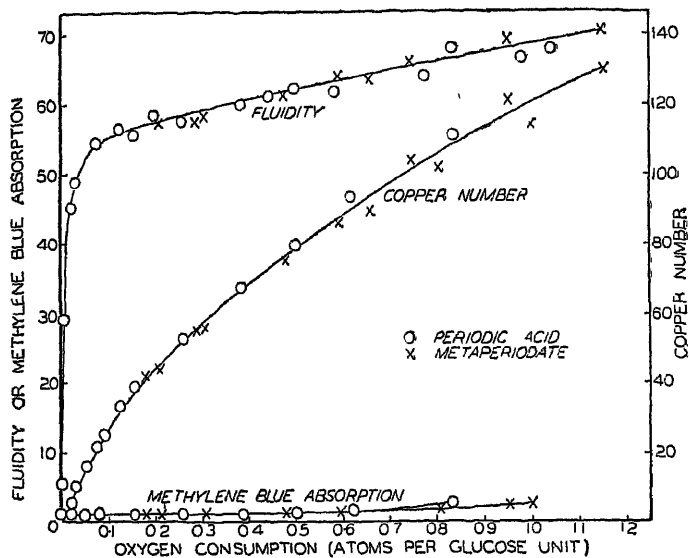


Fig. 1

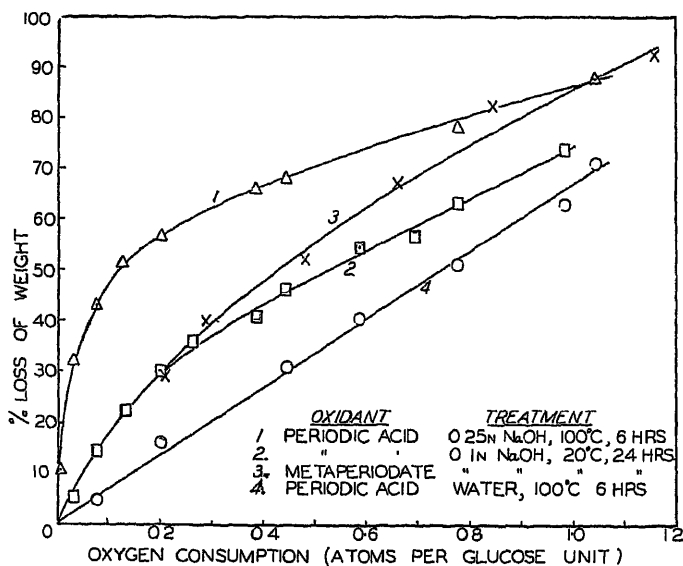


Fig. 2

#### Loss of Weight by Oxycelluloses on Treatment with Dilute Alkali and Hot Water

Curve 1 of Fig 2 illustrates the relation between the proportion of oxygen consumed during the oxidation and the loss of weight that occurs when periodic acid oxycelluloses are treated with 0.25N sodium hydroxide solution for six hours at 100° C. The very considerable loss even in the

early stages of oxidation is what would be expected in view of the highly reducing character of the oxycelluloses. Clibbens, Geake and Ridge<sup>5</sup> have shown that when slightly modified celluloses are boiled with 0.25*N* sodium hydroxide solution for four hours the percentage loss of weight is approximately six times the copper number. This relation holds in the early stages of modification by periodic acid, but it clearly does not hold at high degrees of oxidation, otherwise a loss of 100 per cent would be attained at a copper number of 17 and an oxygen consumption of 0.06 atom per glucose unit.

The relatively slightly modified celluloses hitherto studied suffer only an insignificant loss of weight on treatment with 0.1*N* sodium hydroxide solution for 24 hours at 20° C. Curve 2 of Fig. 2 shows that the loss of weight resulting from this treatment becomes nearly as great as that produced by the action of hot dilute alkali at high degrees of oxidation. At oxygen consumptions less than about 0.2 atom per glucose unit the loss is the same whether oxidation is by periodic acid or metaperiodate, but at higher degrees of oxidation the metaperiodate oxycelluloses (Curve 3) suffer the greater loss.

Boiling with water also produces a notable loss of weight in periodic acid oxycelluloses, the loss on boiling for six hours is almost proportional to the oxygen consumption (Fig. 2, Curve 4), and attains a value of about 65 per cent when the oxygen consumption is one atom per glucose unit.

The solutions obtained by the extraction of highly modified periodic acid oxycelluloses with hot water or with cold or hot alkali were yellow or brown, and displayed reducing power towards alkaline copper solutions. The aqueous extract was acid, and potentiometric titration of the solution obtained by treating an oxycellulose with cold dilute sodium hydroxide solution showed that some of the alkali had been neutralized by acidic products formed in the decomposition of the oxycellulose.

#### **Action of Bisulphite on Oxycelluloses**

Periodic acid oxycelluloses combine with sodium bisulphite in the manner characteristic of carbonyl compounds. When they are treated with a concentrated bisulphite solution, washed and dried, they show an increase of weight that is approximately proportional to the oxygen consumption, and the product yields sulphur dioxide on heating with dilute sulphuric acid. The addition compound is also decomposed by cold dilute sodium hydroxide. In the earlier stages of oxidation the bisulphite compound retains the fibrous form of the oxycellulose, but when the oxygen consumption is high, e.g. one atom per glucose unit, the treated oxycellulose swells to a gel when the bisulphite solution is removed by washing.

#### **Tensile Strength of Oxidized Yarn**

The relation between the tensile strength of cotton yarn oxidized with periodic acid and the proportion of oxygen consumed is illustrated in Fig. 3. The graph shows that the strength falls steeply in the early stages of oxidation, but that beyond an oxygen consumption of about 0.1 atom per glucose unit relatively little further loss of strength occurs. Even after the consumption of 0.7 atom of oxygen per glucose unit the yarn retains 30 per cent of its original strength. At this stage of oxidation the product disintegrates almost immediately in cold 0.1*N* sodium hydroxide solution, and reference to Fig. 2 shows that it would ultimately dissolve to the extent of about 60 per cent. In agreement with the tensile strength data, it is



found that cotton linters does not fall to powder at any stage of its oxidation with periodic acid.

#### Dimensional Changes During Oxidation of Cellulose

It was observed by Jackson and Hudson<sup>1</sup> that when filter paper is highly oxidized with periodic acid it suffers a great contraction in area. This

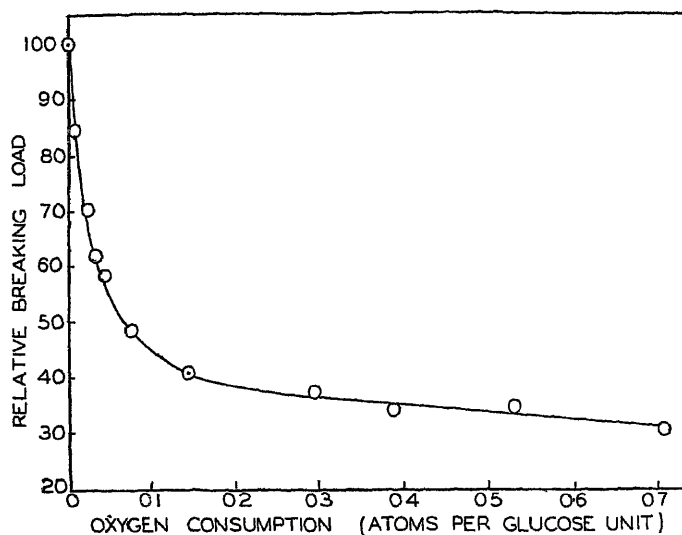


Fig. 3

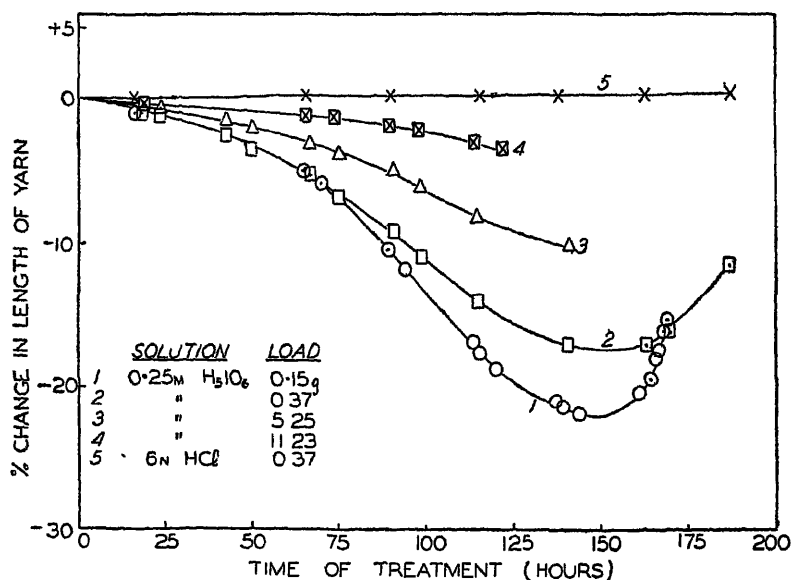


Fig. 4

observation has been confirmed in the present investigation and Table I shows the contraction in area and increase in thickness in relation to oxygen consumption during the oxidation. The measurements were made after the oxidized paper had been washed and dried by exposure to the air.

**Table I**  
**Dimensional Changes in Filter Paper on Oxidation**

Oxygen consumption (atoms per glucose unit)	Relative area	Relative thickness under pressure of		
		1	2	10 lb/sq in
0	100	100	100	100
0.81	62	175	175	174
1.42	28	370	306	260

The shrinkage of cotton yarn during oxidation with periodic acid has also been investigated, and the results obtained are shown graphically in Fig 4 (Curves 1-4). As the oxidation proceeds the yarn gradually shrinks, to an extent that decreases with increasing load, and ultimately breaks. All the curves in Fig 4 are continued to the breaking point, and with the smaller loads it is seen that a considerable and fairly rapid extension occurs immediately before the break. At this stage the yarn has the consistency of a weak jelly. Results obtained in the modification of the same yarn with hydrochloric acid are also included in Fig 4 (Curve 5), and they show that with this reagent the modification proceeds to rupture of the yarn without any important change in length.

#### Hygroscopicity of Oxycelluloses

Periodic acid oxycelluloses are more hygroscopic than unmodified cotton, and their moisture absorption increases progressively with increasing degree of oxidation. Table II shows the relation between the oxygen consumption and the moisture absorption from an atmosphere of 70 per cent. relative humidity.

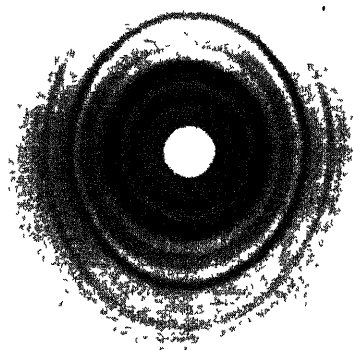
**Table II**  
**Moisture Absorption of Periodic Acid Oxycelluloses at 70 per cent. Relative Humidity**

Oxygen consumption (atoms per glucose unit)	0	0.031	0.077	0.126	0.201	0.444	0.586	0.773	0.982
Moisture absorption (grams water per 100 g dry oxycellulose)	7.9	8.5	8.9	9.2	9.8	11.1	12.3	13.5	14.3
Absorption ratio	1.00	1.08	1.13	1.16	1.24	1.41	1.56	1.71	1.81

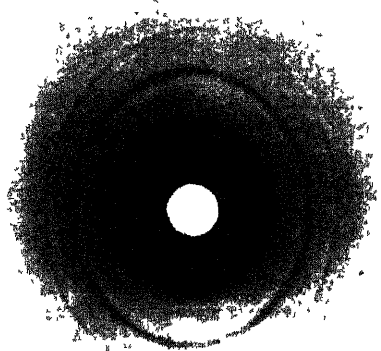
Previous work on the hygroscopicity of chemically modified cottons appears to be confined to that of Urquhart, Bostock and Eckersall<sup>6</sup> with relatively slightly modified hydrocelluloses and alkaline hypobromite oxycelluloses, but with these types the moisture absorption was found to fall with increasing degree of modification.

#### Effect of Oxidation on X-Ray Diagram

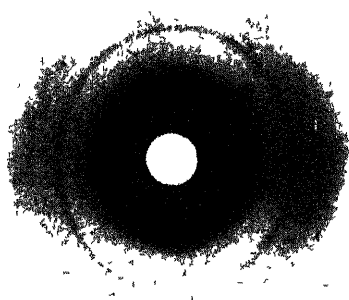
The effect of periodic acid oxidation on the X-ray diagram of cellulose has been investigated on the oxidized filter papers referred to above. The original filter paper gives a good powder diagram. On oxidation no new lines are produced, but the original lines become more diffuse the higher the degree of oxidation (Fig 5). This indicates that no new crystalline structure is produced, and that the original crystalline order is gradually destroyed as oxidation proceeds. The effect of periodic acid oxidation is very different from that of acid attack, for a cotton that has been reduced to powder by the action of concentrated hydrochloric acid gives a very sharp X-ray diagram.



(a)  
Unoxidized filter  
paper



(b)  
Oxidized filter paper,  
oxygen consumption  
= 0.81 atom per  
glucose unit.



(c)  
Oxidized filter paper  
oxygen consumption  
= 1.42 atoms per  
glucose unit

Fig 5 Effect of Periodic Acid Oxidation on X-Ray  
Diagram of Cellulose

**Nitrogen Content of Nitrocelluloses Derived from Oxycelluloses**

Evidence regarding the proportion of the hydroxyl groups that is destroyed by oxidation of cellulose may be obtained by nitrating the oxycelluloses under conditions that lead to substantially complete esterification and comparing the nitrogen content of the nitrocelluloses so obtained with that of the nitrocellulose derived from the unoxidized cellulose.<sup>7, 8</sup> This method has been applied to oxycelluloses prepared by the action of periodic

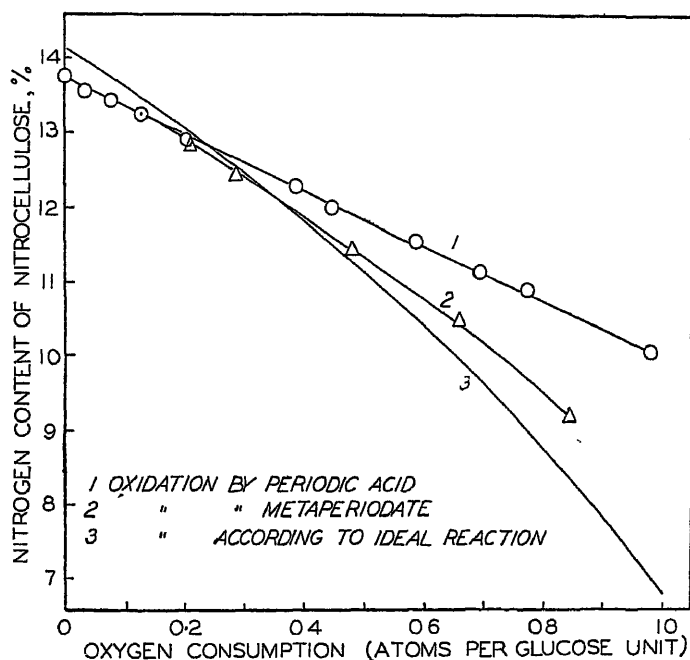


Fig 6

acid and metaperiodate, with results that are illustrated in Fig 6. It is seen that with progressive increase of the proportion of oxygen consumed in the formation of the oxycellulose the nitrogen content of the derived nitrocellulose falls steadily, and that this fall is greater when metaperiodate is the oxidant than when periodic acid is used.

**The Solubility in Acetone of Nitrocelluloses Derived from Oxycelluloses**

In the study of the early stages of cellulose modification the measurement of the fluidity in acetone solution of nitrocelluloses derived from the modified celluloses has played a prominent part.<sup>3, 9</sup> This measurement is not possible on materials oxidized with periodic acid beyond a certain point, since the nitrocelluloses derived from them are found to be incompletely soluble in acetone. Curve 1 of Fig 7 shows that when the oxygen consumption increases beyond about 0.02 atom per glucose unit the fractional solubility of the nitrocellulose falls very steeply to low values. This behaviour is not due to low nitrogen content, for a nitrocellulose that dissolves only to the extent of 10 per cent. has a nitrogen content of 13.4 per cent.—a value that would normally confer complete solubility in acetone. Curve 2 of Fig 7 shows that when the oxycelluloses are prepared from a hydrocellulose instead of from an unmodified cotton the fractional solubility

of the derived nitrocellulose for a given degree of oxidation is considerably increased

#### Production of Carbon Dioxide and Loss of Weight During Oxidation of Cellulose

It has been found that when cellulose is oxidized with periodic acid or metaperiodate a certain proportion of carbon dioxide is produced. Table III gives the yield of carbon dioxide and the concomitant loss of weight by the cellulose in relation to the oxygen consumption

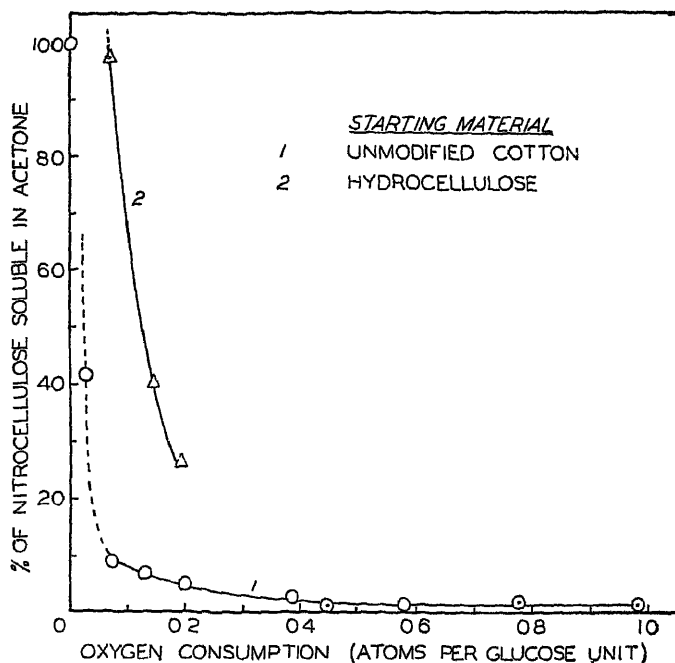


Fig 7

Both the yield of carbon dioxide and the loss of weight increase with increasing degree of oxidation, and both are considerably greater in periodic acid oxidation than in metaperiodate oxidation.

**Table III**  
**Yield of Carbon Dioxide and Loss of Weight in the Oxidation of Cellulose**  
(1 gram cotton in 100 c.c. oxidant, at 20-21° C.)

Concentration of oxidant (moles/l )	Time of oxidation (hours)	Oxygen consumption (atoms per glucose unit)	Loss of weight, %	Yield of carbon dioxide	
				%	Molecules per glucose unit
Periodic acid					
0.0905	72	0.324	3.0	0.28	0.010
0.0915	168	0.616	6.2	1.06	0.039
0.0942	168	0.661	6.8	—	—
0.0937	185	0.693	6.4	—	—
0.0908	336	1.045	8.9	2.60	0.096
Metaperiodate					
0.0980	72	0.436	0.6	0.15	0.006
0.0909	170	0.701	1.0	0.26	0.010
0.0991	141	0.744	1.6	0.46	0.017
0.0991	285	0.950	1.5	0.64	0.024

### Production of Formic Acid and Formaldehyde During Oxidation of Cellulose

Examination of periodic acid and metaperiodate solutions that had been used to oxidize cellulose revealed that, as in many other oxidations with these substances, formic acid and formaldehyde are formed during the oxidation process. The production of an acid stronger than carbonic acid was established, and the amount of the acid determined, by potentiometric titration of solutions before and after their use in the oxidation of cellulose. A quantitative separation of this acid was obtained by distillation under reduced pressure at 30° C., and a determination of its dissociation constant by potentiometric titration indicated that the acid was formic acid. This identification was confirmed by the crystalline form and the analysis of the lead salt of the acid. Formaldehyde was identified and estimated by means of its condensation product with dimedone (dimethylcyclohexanedione).

Table IV gives the yields of formic acid and formaldehyde obtained in a number of oxidations. It shows that the proportion of formic acid produced increases with the degree of oxidation of the cellulose, and that much more is produced in oxidation with periodic acid than with metaperiodate. The yield of formaldehyde is much less than that of formic acid, the ratio being about 1 to 6.

In the extensive work that has been done on the oxidation of polyhydroxylic compounds it seems to have been tacitly assumed that formic acid and formaldehyde, the characteristic products of these reactions, are themselves stable towards periodic acid. Experiment has shown, however, that both these substances suffer appreciable oxidation during the long periods of a week or more necessary for the production of a high degree of oxidation in cellulose, the rate of oxidation of formaldehyde being greater than that of formic acid.

Table IV  
Yields of Formic Acid and Formaldehyde in the Oxidation of Cellulose (20° C.)

Concentration of oxidant (moles/l.)	Grams of cotton per 100 c.c. of oxidant	Time of oxidation (hours)	Oxygen consumption (atoms per glucose unit)	Yield (molecules per glucose unit)	
				Formic acid	Formaldehyde
Periodic acid					
0.0952	1.10	67	0.264	0.018	—
0.0938	0.96	168	0.661	0.170	—
0.0934	1.00	185	0.693	0.178	—
0.0954	"	358	0.934	0.209	0.035
0.0956	1.02	479	1.042	0.226	—
Metaperiodate					
0.0938	2.00	24	0.207	0.004	—
"	"	92	0.478	0.020	—
"	"	188	0.658	0.030	—
0.0909	1.00	163	0.803	0.039	0.006
0.0951	"	262	0.942	0.039	—
0.0912	"	259	1.001	0.052	0.008

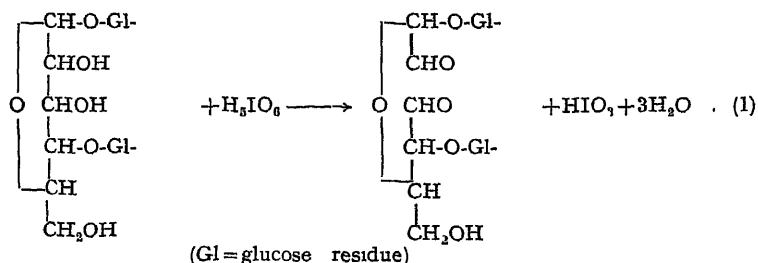
### The Possibility of Hydrolysis During the Oxidation Process

In order to obtain high degrees of oxidation with periodic acid, treatment of cellulose with the oxidant for long periods is necessary, and it seemed possible that this prolonged treatment with an acid solution might result in a certain amount of hydrolysis of glycosidic linkages. The acidity

during the oxidation with periodic acid is partly due to the stronger acid, iodic acid, produced by the reduction of periodic acid, and the effect of treatment of an unmodified cotton with iodic acid (which does not oxidize cellulose) has been employed as an index of possible hydrolysis during periodic acid oxidation. It was found that treatment of the cotton with 0.2*M* iodic acid for 288 hours at 20° C. increased the fluidity in cuprammonium solution from 5.6 to 9.2, indicating a very slight degree of acid attack. Results previously given<sup>3</sup> suggest that the susceptibility of a cotton to acid attack is not greatly increased by oxidation with periodic acid, and this conclusion is supported by further work on a more highly oxidized product; an oxycellulose formed by an oxygen consumption of 1.04 atom per glucose unit lost only 2.9 per cent of its weight on treatment with 5.5*N* hydrochloric acid for 24 hours at 20° C., whereas the corresponding loss on treatment with 0.1*N* sodium hydroxide was about 75 per cent. These results lead to the conclusion that acid hydrolysis does not play an important part in the oxidation of cellulose by periodic acid. The possibility of acid attack during oxidation with metaperiodate may be ruled out on account of the very low hydrogen ion concentration of metaperiodate solutions.

#### DISCUSSION

According to Jackson and Hudson<sup>2</sup>, the main reaction in the oxidation of cellulose by periodic acid is the cleavage of the carbon chains in the glucose units between carbon atoms 2 and 3 and the conversion of the secondary alcohol groups to aldehyde groups, as represented by the equation



This reaction, which in the following discussion will be termed the ideal reaction, is what would be expected from the known behaviour of periodic acid with polyhydric alcohols and with the methyl hexosides in particular. Jackson and Hudson have shown that it at least plays a part in the oxidation of cellulose by proving that glyoxal and erythrose are formed by hydrolysis of the oxidation product, but these substances—or their derivatives—were obtained in relatively small (15-20 per cent) yields<sup>2</sup>. According to the ideal reaction, the oxidation should be complete when one atom of oxygen per glucose unit has been consumed, but Jackson and Hudson<sup>1</sup> followed the oxidation to almost double this oxygen consumption. The work of these investigators thus suggests that the above equation does not suffice completely to describe the oxidation of cellulose by periodic acid. The present investigation provides ample evidence in support of this conclusion.

The high reducing power and low affinity for Methylene Blue displayed by the periodic acid oxycelluloses and the ability of the latter to combine with bisulphite are in accord with the aldehydic character of the oxidation product formulated in equation (1). The inadequacy of this equation as a

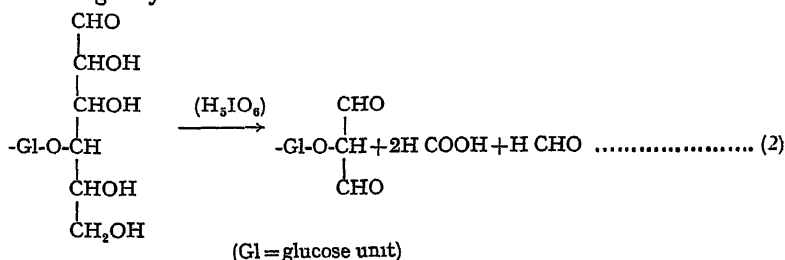
complete representation of the action of periodic acid on cellulose is, however, made clear by the considerable yields of formaldehyde, formic acid and carbon dioxide that have been found and also by the loss of weight suffered by the cellulose during oxidation (Tables III and IV). Jackson and Hudson<sup>1</sup> have reported yields of the oxycellulose in agreement with that calculated from the equation, but this has not been confirmed in the present investigation. Whereas the calculated loss of weight when an atom of oxygen has been consumed by every glucose unit is 1.2 per cent., the loss observed at an oxygen consumption of 1.05 atom per glucose unit was 8.9 per cent. For a given degree of oxidation of the cellulose the loss of weight and the yields of formaldehyde, formic acid and carbon dioxide are considerably smaller in metaperiodate than in periodic acid oxidation, suggesting that the former process approximates more closely to the ideal reaction than the latter.

Evidence that the oxidation process is less simple than that represented by equation (1) is also provided by the data relating to the nitrogen content of the nitrocelluloses derived from the oxycelluloses. If the oxidation process is confined to the ideal reaction, then the nitrogen content corresponding to complete nitration of the product may be calculated at any stage of the oxidation; it is given by the equation

$$\%N = \frac{1401 (3 - 2x)}{205.1x + 297.1(1 - x)}$$

where  $x$  is the number of atoms of oxygen consumed per glucose unit. In Fig. 6 the observed relation between nitrogen content and oxygen consumption is compared with the calculated relation, and it is seen that at high degrees of oxidation the nitrogen contents of nitrocelluloses prepared from periodic acid oxycelluloses (Curve 1) are considerably higher than the calculated values (Curve 3). This indicates that the oxycelluloses contain more hydroxyl groups than the product of the ideal reaction, and that oxygen must have been consumed in ways other than the conversion of secondary alcohol groups to aldehyde groups. Fig. 6 also shows that the relation between nitrogen content and oxygen consumption is nearer to the calculated relation when metaperiodate (Curve 2) is the oxidant than when periodic acid is used, and this supports the conclusion already reached that the oxidation of cellulose by metaperiodate diverges less from the ideal reaction than does oxidation by periodic acid.

The reaction represented by equation (1) refers only to the non-terminal glucose units in the molecular chains of cellulose, and the terminal units would be expected to react in a different manner. The non-reducing terminal unit should, by analogy with the methyl hexosides, yield one molecule of formic acid, and the reducing terminal unit should, by analogy with glucose, yield both formic acid and formaldehyde. Caldwell and Hixon<sup>10</sup> have formulated the oxidation of a reducing terminal glucose unit in the following way:—





and have made this equation the basis of an attempt to calculate the molecular chain-length of starch from the yield of formaldehyde produced by periodic acid oxidation. When a similar calculation is made from the yield of formaldehyde obtained from the oxidation of cellulose (Table IV) a value of 29 glucose units is obtained for the average chain-length of the cotton used. Similarly, the degree of polymerization may be calculated from the maximum formic acid yield on the assumption that the oxidation of the two terminal glucose units in each chain-molecule yields 3 molecules of formic acid; this calculation leads to a chain-length of 13 glucose units. There is, however, abundant evidence to show that the molecular chains of a cotton such as was used in these oxidations contain many hundreds of glucose units, so that it is evident that the yields of formaldehyde and formic acid obtained cannot be accounted for by the oxidation of the terminal glucose units in the manner postulated by Caldwell and Hixon. It is possible that the attack on the reducing ends of the chain-molecules is not confined to the terminal glucose unit, but leads to a progressive shortening of the molecular chains by a kind of erosion from the end. There also exists the alternative possibility that the excessive loss of weight and the production of formaldehyde, formic acid and carbon dioxide result from reactions which follow the primary attack on the non-terminal units.

According to the ideal reaction represented by equation (1), the linkages uniting the original glucose units in the chain-molecules of cellulose should not be broken by oxidation with periodic acid. Previous work on the oxycelluloses formed in the early stages of the oxidation has indicated that the action of this oxidant produces relatively little immediate scission of chain-molecules, but that linkages in the latter are rendered very susceptible to cleavage by alkalis.<sup>8</sup> These alkali-sensitive linkages are broken by the alkaline solvent during the measurement of fluidity in cuprammonium solution, with the result that the fluidity is much higher than corresponds to the average chain-length in the oxidized fibre before dissolution. The manner in which the oxidized chain-molecule is broken by the action of alkalis is still obscure, but it has been suggested that the glycosidic linkage attached to carbon atom 4 of a glucose unit that has been oxidized according to equation (1) would be susceptible to alkaline hydrolysis.<sup>9</sup> Oxidation according to the ideal reaction with production of alkali-sensitive linkages might be expected to yield a product that would undergo complete depolymerization on dissolution in cuprammonium and show a fluidity not appreciably lower than that of the solvent. The fluidity actually found at an oxygen consumption of one atom per glucose unit is about 68.5 compared with 72 for the solvent, and calculation of the mean chain-length from these figures by means of Staudinger's equation yields a value of 20 or 26 glucose units, according as the constant given by Staudinger and Daumiller<sup>11</sup> or by Kraemer and Lansing<sup>12, 13</sup> is employed.

The large losses of weight suffered by periodic acid oxycelluloses under the action of cold dilute sodium hydroxide or boiling water are also to be attributed to the presence of alkali-sensitive linkages. With the very slightly modified materials previously studied the losses of weight produced by these treatments are negligibly small, but as the proportion of alkali-sensitive linkages progressively increases by reason of increasing degree of oxidation it is to be expected that the rupture of these linkages will give rise to soluble products in increasing amount. The loss of weight produced by the action

of hot dilute sodium hydroxide on periodic acid oxycelluloses is probably due in part to the rupture of alkali-sensitive linkages as with cold alkali, but also in part to chemical changes associated with the destruction of reducing groups and similar to those which occur when hydrocelluloses are boiled with alkali.

According to a conception of the fine structure of cellulose that is now widely accepted, fibrous cellulose is built up from long molecular chains lying roughly parallel to each other, with here and there regions where the arrangement has attained crystalline order. On this view, the crystalline regions have no sharp boundaries, but consist of portions of chain-molecules that after passing through amorphous inter-crystalline regions may take part in the structure of other crystalline regions. It is generally assumed that the crystalline portions of the fibre are not penetrated by water or dilute aqueous solutions, and that the absorption of moisture and chemical attack by dilute solutions of acids and oxidizing agents occur only in the amorphous regions. It has been seen, however, that on progressive oxidation of cellulose with periodic acid the lines in the X-ray diagram of the cellulose become more and more diffuse (Fig 5), suggesting that in this case the originally crystalline regions are gradually opened up and made accessible to the oxidizing agent. This conclusion is also supported by the great dimensional changes and the enhanced hygroscopicity that result from the oxidation. It seems unlikely that the aldehyde groups produced by the oxidation will have a greater affinity for moisture than the hydroxyl groups they replace, whereas the opening up of the crystalline regions would render more of the hydrophilic groups accessible to moisture.

Nitrocelluloses with nitrogen contents greater than about 10 per cent are usually soluble in acetone, and the abnormal behaviour in this respect of the nitrocelluloses derived from periodic acid oxycelluloses therefore merits discussion. A nitrocellulose prepared from an unmodified cotton by the method employed in this investigation consists of very long molecular chains in which nearly all the hydroxyl groups of the original cellulose have been replaced by nitrate groups. These chains are held together by the mutual attraction of the nitrate groups on adjacent chains, and the solubility of such a nitrocellulose is due to the greater attraction of these groups for acetone than for each other. A nitrocellulose similarly derived from a periodate oxycellulose is presumed to differ only in possessing a slightly smaller mean chain-length and in having a number of aldehyde groups distributed along its chain-molecules. Hence in order to account for the insolubility of the latter nitrocellulose it seems necessary to assume that the detachment of the chain-molecules from each other which is necessary for dissolution is prevented by the attractive forces between aldehyde groups, or between aldehyde and nitrate groups, on neighbouring chain-molecules. The insolubility is not complete when the proportion of aldehyde groups is small, however, and this may be attributed to the dissolution of the shorter chains which do not possess the minimum number of aldehyde groups necessary to prevent their detachment from their neighbours. As the degree of oxidation of the parent oxycellulose increases, even the shortest chain-molecules attain this minimum number and the fractional solubility falls practically to zero. Similar considerations would explain the observation, illustrated in Fig 7, that when the average chain-length is reduced by preparing the parent oxycellulose from a hydrocellulose instead of from an

unmodified cotton the fractional solubility of the nitrocellulose for a given degree of oxidation is considerably increased.

## Materials

## EXPERIMENTAL

The cellulosic materials that were oxidized were: (1) a sample of cotton linters that had been purified industrially by boiling under pressure with dilute sodium hydroxide; (2) a 3/90's gassed, super-combed hosiery yarn, boiled for  $5\frac{1}{2}$  hours with 2 per cent sodium hydroxide solution at a pressure 40 lb /sq. in in excess of atmospheric, and bleached by treatment for an hour with  $N/25$  sodium hypochlorite at pH 11.3 (3) Whatman filter paper, No 44; and (4) a hydrocellulose prepared from the linters by the action of hydrochloric acid (200 g /litre) at 20° C. Most of the work was done with the cotton linters, this material being used except where otherwise stated

The periodic acid solutions used as oxidants were for the most part prepared from various samples of the crystalline acid, but in a few instances they were prepared from re-crystallized sodium metaperiodate by the addition of an equivalent of sulphuric acid. The samples of the acid contained from 91 to 95 per cent of the amount of periodic acid required by the formula  $H_5IO_6$ , and all contained a certain amount of iodic acid or iodate. Sodium metaperiodate solutions were prepared from periodic acid by the addition of sodium hydroxide in the proportion of 1 mole of alkali per mole of acid, or from the re-crystallized salt

## Methods of Oxidation

The oxidants employed were solutions of periodic acid with concentrations up to 0.25M (0.5N as oxidizing agent) and approximately 0.1M solutions of sodium metaperiodate. The ratio of cellulose to oxidizing solution was usually 1 gram per 100 c.c., but in a few cases this was increased to 2 grams per 100 c.c. The cellulose was oxidized in conical flasks provided with ground-in glass stoppers, and the flasks were shaken at intervals. Most of the oxidations were performed in a thermostat at 20° C., but a few were carried out at room temperature. The oxidized celluloses were washed to neutrality with cold distilled water and dried by exposure to the air.

## Determination of Oxygen Consumption

The oxygen consumption during the oxidation was calculated from the fall in the periodate concentration, after allowing for any fall due to spontaneous decomposition of the oxidant. This correction, which was always very small, was obtained from a blank experiment. The concentration of the periodate solutions was determined by adding sodium bicarbonate solution, followed by potassium iodide solution, and titrating the liberated iodine with standard arsenite solution<sup>14</sup>. This method was found to give the same result as the less direct method of Fleury and Lange<sup>15</sup>, in which the periodate is reduced by an excess of standard arsenite in the presence of sodium bicarbonate, and the excess arsenite back-titrated with iodine solution. The object of this latter method was to avoid the reduction of iodine by formaldehyde which was thought to be possible if the direct method was applied to periodic acid solutions that had been used to oxidize substances yielding formaldehyde. It has been found, however, that a proportion of formaldehyde much greater than those present in solutions that have been used to oxidize cellulose does not interfere in the direct

method, provided the titration is carried out immediately after the liberation of the iodine.

### Properties of Oxycelluloses

*Fluidity in cuprammonium solution* Measurements of the fluidity of oxycelluloses were made by the method of Clibbens and Geake,<sup>16, 17, 18</sup> but fluidities higher than about 35 were determined in a modified form of the standard viscometer with a longer and narrower capillary in order to keep the kinetic energy corrections low. The chemical instability of the periodic acid oxycelluloses towards cuprammonium was shown with the more highly oxidized products by a darkening of the solutions after several hours and by the subsequent formation of a precipitate. With these materials the measurement of fluidity was therefore made after four hours from the addition of the cuprammonium to the oxycellulose instead of after the period of 16-20 hours usually allowed. The values recorded are the fluidities in c g s. units of 0.5 per cent solutions at 20° C.

The results obtained are given in Table V and the relation between fluidity and oxygen consumption is shown graphically in Fig. 1.

*Copper number.* The copper numbers of oxycelluloses were determined by the method described by Clibbens and Geake<sup>19</sup>, but, owing to the wide range of reducing power to be covered, it was necessary to vary the ratio of modified cotton to copper solution between the limits of 2.5 and 0.05 g. per 100 c c.

The relation between copper number and oxygen consumption is shown in Table V and Fig. 1.

*Methylene Blue absorption* The absorption of Methylene Blue was determined by the titrimetric method described by Birtwell, Clibbens and Ridge<sup>20</sup>, a solution of the dye buffered at pH 7 being employed<sup>21</sup>. The results given are based on the absorption by 1 gram of oxycellulose from 15 c c of 0.004M solution and are expressed as millimoles of Methylene Blue absorbed per 100 g of dry oxycellulose.

The variation of the Methylene Blue absorption with the oxygen consumption is shown in Table V and Fig. 1.

*Loss of weight on treatment with cold and hot sodium hydroxide solution and with hot water* Determinations were made of the loss of weight suffered by oxycelluloses as the results of treatment with (a) 0.1N sodium hydroxide solution at 20° C. for 24 hours, (b) water at 100° C. for 6 hours, (c) 0.25N sodium hydroxide solution at 100° C. for 6 hours. The methods employed in the three determinations were essentially the same. About 0.3 gram of the oxycellulose, previously dried to constant weight in vacuo over phosphorus pentoxide, was treated in a 100 c c. conical flask filled to the neck with solution or water, the flask, stoppered for treatments at 20° C or closed with a pear-shaped bulb for treatments at 100° C, being immersed to the neck in a thermostat at 20° C or a vigorously boiling water-bath. The residue was then collected in a fritted-glass filter-crucible (G3), acidified with dilute acetic acid in the case of the alkaline treatments, washed to neutrality, and dried to constant weight at 110° C.

The results of determinations of loss of weight by oxycelluloses are included in Table V, and the relations between oxygen consumption and loss of weight are illustrated in Fig. 2.

Table V  
Properties of Periodic Acid and Metaperiodate Oxycelluloses

Oxygen consumption (atoms per glucose unit)	Fluidity in cuprammonium	Copper number	Methylene Blue absorption	% Loss of weight on treatment with			Derived nitrocellulose	
				Water at 100° C for 6 hours	0.1N NaOH at 20° C for 24 hours	0.25N NaOH at 100°C for 6 hours	% Nitrogen	% Soluble in acetone
Unmodified cotton (inters)      Periodic acid								
0	5.6	0.14	1.18	—	—	1.0	13.73	100.0
0.0052	29.2	1.62	—	—	0.5	10.5	13.66	100.0
0.0207	45.2	5.60	1.13	—	—	—	—	—
0.0308	48.8	10.2	1.10	—	5.5	32.1	13.57	41.7
0.0527	—	15.8	1.08	—	—	—	—	—
0.0765	54.5	21.7	1.08	4.8	14.7	43.0	13.44	9.2
0.0920	—	24.9	1.08	—	—	—	—	—
0.126	56.3	33.4	—	—	22.4	51.2	13.26	6.8
0.156	55.6	39.0	1.01	—	—	—	—	—
0.201	58.6	—	—	16.2	30.1	56.7	12.90	4.9
0.260	57.7	52.8	1.09	—	36.4	—	—	—
0.386	60.0	67.4	1.28	—	41.0	66.1	12.27	2.8
0.444	61.2	—	—	31.0	46.6	68.0	11.99	1.3
0.499	62.3	79.4	1.38	—	—	—	—	—
0.586	61.8	—	—	40.5	54.0	—	11.56	1.4
0.621	—	93.3	1.70	—	—	—	—	—
0.693	—	—	—	—	56.8	—	11.16	—
0.773	63.9	—	—	51.1	63.2	78.2	10.90	1.8
0.833	67.9	110.8	2.87	—	—	—	—	—
0.982	66.7	—	—	65.1	73.9	—	10.07	1.3
1.042	67.9	—	—	71.4	—	88.2	—	—
Hydrocellulose      Periodic acid								
0	36.9	—	—	—	—	—	13.70	100.0
0.068	52.0	—	—	—	10.2	—	13.46	97.5
0.145	54.5	—	—	—	19.8	—	13.30	40.5
0.193	55.5	—	—	—	24.0	—	13.16	26.2
Unmodified cotton (inters)      Sodium metaperiodate								
0.180	—	41.7	1.04	—	—	—	—	—
0.208	57.3	43.6	1.09	—	29.1	—	12.86	3.3
0.286	57.5	54.9	—	—	40.1	—	12.44	—
0.306	58.2	55.4	1.13	—	—	—	—	—
0.478	61.1	75.2	1.26	—	52.2	—	11.44	—
0.594	64.0	85.8	1.37	—	—	—	—	—
0.658	63.5	89.1	—	—	67.0	—	10.51	—
0.745	66.0	103.7	—	—	—	—	—	—
0.805	—	101.6	1.94	—	—	—	—	—
0.843	—	—	—	—	82.6	—	9.21	—
0.950	69.2	120.9	2.59	—	—	—	—	—
1.000	—	114.0	2.76	—	—	—	—	—
1.153	70.6	129.7	—	—	92.6	—	—	—

*Increase of Weight on Treatment with Bisulphite.* About 0.35 gram. of the oxycellulose, previously dried over phosphorus pentoxide and weighed, was treated for 24 hours at 20° C with 100 c.c. of a solution of sodium bisulphite (180 g./litre). The treated oxycellulose was then collected in a fritted-glass filter-crucible (G3), washed, and dried to constant weight over phosphorus pentoxide. This determination was not practicable with an oxycellulose formed by the consumption of one atom of oxygen per glucose unit, owing to the formation of a gel when the treated oxycellulose was washed.

The increase of weight in relation to the oxygen consumption is given in Table VI.

**Table VI**  
**Increase of Weight on Treatment of Oxycelluloses with Bisulphite**

Oxygen consumption (atoms per glucose unit)	0	0.126	0.201	0.444
Per cent change of weight of oxycellulose	-0.1	+7.6	+9.8	+19.1

*Hygroscopicity.* The hygroscopicities of oxycelluloses were compared by determining their moisture absorptions from an atmosphere of 70 per cent. relative humidity at 20° C. The samples, weighing about 0.3 gram and contained in weighing-bottles, were dried to constant weight in vacuo over phosphorus pentoxide. They were then kept in an evacuated desiccator containing sulphuric acid solution of the required concentration (33g/100g solution) until their weights became constant.

The results obtained have already been given in Table II.

#### Preparation and Properties of Nitrocelluloses Derived from Oxycelluloses

Nitrocelluloses were prepared from periodic acid and metaperiodate oxycelluloses by nitration with a mixture of nitric acid, phosphoric acid and phosphorus pentoxide, according to the procedure previously described.<sup>1</sup> This method of nitration gives almost complete esterification of an unmodified cotton, and it is believed that it produces little, if any, degradation.

The nitrogen contents of the nitrocelluloses were determined by the modified Devarda method, the details being as previously described.<sup>1</sup>

The percentage of a nitrocellulose that was soluble in acetone was determined by agitating a known weight of nitrocellulose with a known volume of acetone for 18 hours, centrifuging down the undissolved material, and evaporating an aliquot portion of the solution to dryness at 65° C. Determinations by this method with nitrocelluloses that were completely soluble indicated that about 4 per cent. of acetone was retained by the dried residue, and all the results have been corrected accordingly. The behaviour of the incompletely soluble nitrocelluloses when acetone was added was strikingly different from that shown by the completely soluble, whereas with the latter the mass of fibres coalesced to form a transparent gel, with the former it broke up into separate fibres, which appeared swollen when the solubility was still considerable but unswollen when the solubility was very small.

The nitrogen contents and solubilities of the nitrocelluloses are recorded in Table V, and the variation of these properties with the oxygen consumption of the parent oxycellulose is shown graphically in Figs. 6 and 7.

#### Tensile Strength of Oxidized Yarns

The effect of periodic acid oxidation on the tensile strength of cellulose was investigated by determining the mean single-thread breaking load of a sample of cotton yarn and nine similar samples that had been oxidized to various degrees. The yarn samples were prepared by the "cut-skein" method.<sup>22</sup> Each sample contained 100 threads, and the breaking load was measured on 15 cm. lengths. The measurements were made with the Goodbrand single-thread tester, at a temperature of 65–70° F. and a relative humidity of 65 per cent.

The results obtained are given in Table VII and shown graphically in Fig. 3.

**Table VII**  
**Relation between Degree of Oxidation and Tensile Strength**

Oxygen consumption (atoms per glucose unit)										
0	0.0079	0.023	0.034	0.042	0.075	0.143	0.294	0.383	0.531	0.707
Relative breaking load										
100	84.6	70.1	61.5	58.2	48.4	40.8	37.5	34.4	34.8	30.9

#### Shrinkage of Filter Paper and Cotton Yarn during Oxidation

The dimensional changes in filter paper recorded in Table I were measured on squares of No. 44 Whatman filter paper (3.5 cm × 3.5 cm) that were oxidized with 0.094M periodic acid solution.

Measurements of the length changes resulting from the action of periodic and hydrochloric acid on cotton yarn were made in a glass tube of circular section at the ends but flattened over most of its length so as to give two approximately plane faces. Along these plane faces was etched a millimetre scale which served to measure the length of the yarn. The top end of the tube was closed by a rubber stopper, and the lower end was sealed to glass tubing of narrower bore which was closed by a piece of rubber tubing and screw clip. A loop of yarn about 35 cm long was suspended from a glass hook attached to the stopper and was kept taut by a weight made from nickel wire or stainless steel sheet; the flat shape of these weights also prevented untwisting of the yarn. The length of the yarn was measured immediately after the immersion of the yarn in the solution, and at suitable intervals during the course of the oxidation or hydrolysis. The results obtained have been shown graphically in Fig. 4.

#### Determination of Loss of Weight by Cellulose during Oxidation

The cotton, dried in vacuo over phosphorus pentoxide and weighed, was oxidized and washed to neutrality with cold water, the washings being filtered through a fritted-glass filter-crucible. The oxycellulose was finally transferred to the filter-crucible and dried to constant weight as before.

The results are given in Table III.

#### Estimation of Carbon Dioxide Produced by Oxidation of Cellulose

In the estimation of the carbon dioxide produced in the oxidation of cellulose by periodic acid the oxidation was conducted in the apparatus illustrated in Fig. 8(a), and the carbon dioxide formed was subsequently absorbed in standard alkali in the apparatus shown in Fig. 8(b). In this latter apparatus, which is essentially the same as that described by Reid and Weihe<sup>22</sup>, the absorber consists of a glass tube 70 cm long, with an internal diameter of 1.4 cm, having a fritted-glass disc sealed into its lower end. This tube passes through a rubber stopper that fits into the neck of a 250 c.c. filter flask, the joint between the tube and the stopper being lubricated with glycerol. When suction is applied at the top of this tube, a current of air is drawn in through the side-tube of the filter flask and bubbles up through a tall column of alkali standing in the tube. The addition of a drop of amyl alcohol to the alkali promotes the formation of smaller bubbles.

About 0.75 gram of cotton, previously dried to constant weight over phosphorus pentoxide, was oxidized at 20–21° C. with 75 c.c. of approximately M/10 periodic acid in the reaction flask, the ground joint and taps being lubricated with tap-grease and the air pressure in the flask reduced below atmospheric at the beginning of the oxidation. At the end

of the required time of oxidation the reaction flask was connected to the absorption apparatus by rubber tubing, and the carbon dioxide swept out by means of a brisk current of air free from carbon dioxide and absorbed in 50 c.c. of  $N/20$  sodium hydroxide in the absorption tube. After an hour the air current was stopped, the absorption tube raised by sliding it in the rubber stopper, and the alkali allowed to drain into the flask. The absorption tube was then washed with two 25 c.c. portions of water, each portion being allowed to run through into the flask. After removal of the absorption tube, 10 c.c. of 15 per cent. barium chloride solution and a few drops of phenolphthalein were added to the solution in the filter flask, and the excess sodium hydroxide titrated with  $N/10$  hydrochloric acid. In this titration a burette with a long jet was used, the tip of the jet being immersed in the solution to be titrated. The procedure for the absorption and determination of carbon dioxide was then repeated, the air current being passed for a further period of half-an-hour to ensure that all the carbon dioxide had been swept out of the reaction flask. The sodium hydroxide solution was standardized by means of a blank experiment. It was shown that formic acid present in the reaction flask in concentrations such as are produced during the oxidation of cellulose did not interfere in the determination of carbon dioxide.

Results relating to the production of carbon dioxide during the oxidation of cellulose by periodic acid and metaperiodate are given in Table III

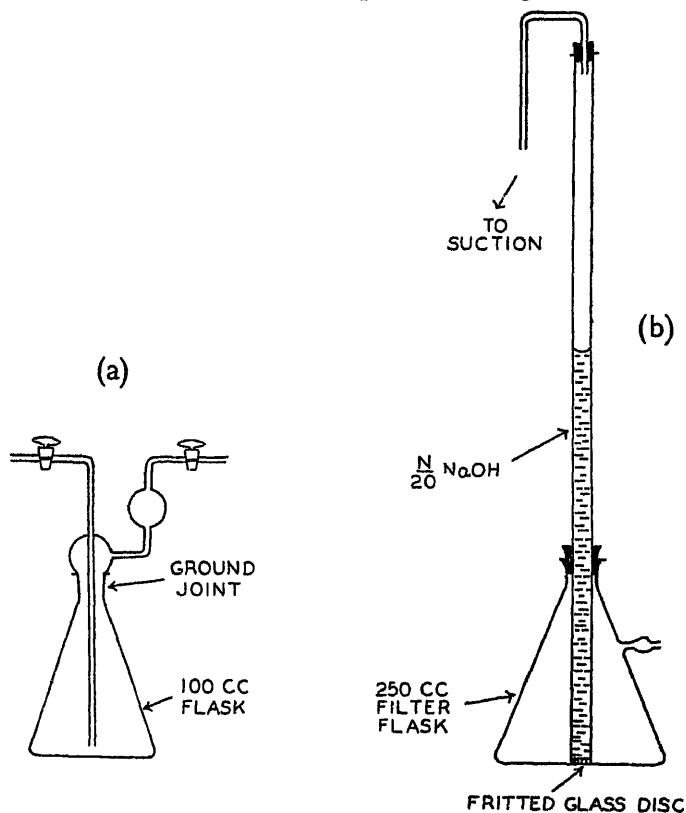


Fig 8



# **Identification and Estimation of Formic Acid Produced by Oxidation of Cellulose**

Periodic acid is a polybasic acid, and the first break in its titration curve occurs at  $pH$  5.3, corresponding to the formation of metaperiodate. The reduction of periodic acid by cellulose results in the formation of the stronger monobasic acid, iodic acid, and the carbonic acid produced in the oxidation of cellulose is neutralized to only a slight degree at  $pH$  5.3, so that if no organic acid is produced by the oxidation of cellulose the amount of alkali required to bring the oxidizing solution to  $pH$  5.3 should remain substantially unchanged. Potentiometric titration, by means of the glass electrode, of a solution that had been used to oxidize cellulose showed, however, that more alkali than before was required to bring the solution to  $pH$  5.3, and there was still a sharp break at this  $pH$  value, indicating that the acid produced had little buffer action in this region. Hence, apart from the slight error due to the fact that the neutralization of the organic acid may not be quite complete at  $pH$  5.3, the amount of acid produced may be calculated from the results of titrations to  $pH$  5.3 before and after oxidation. Similarly, when metaperiodate is used as oxidant the production of acid will lower the  $pH$  from its initial value of 5.3, and the amount of alkali required to restore the initial value will give the amount of acid produced.

In an attempt to isolate the organic acid produced during the oxidation of cellulose by periodic acid, portions of a solution that had been used to oxidize cellulose were distilled under reduced pressure at  $30^{\circ}C$ . The condenser and receiver were cooled by a current of water at about  $10^{\circ}C$ . and by immersion in crushed ice, respectively, and the distillation was carried almost to dryness. The distillate was acid, and after neutralization and concentration it gave the reactions of formic acid, for example, the neutral solution reduced silver nitrate and mercuric chloride. That the acid in the distillate was formic acid was confirmed by a comparison of its titration curve, determined by means of the glass electrode, with that of a specimen of formic acid. The curves relating percentage neutralization and  $pH$  were almost coincident, and the derived  $pK$  values were 3.81 and 3.84 for the distillate and formic acid respectively. The concentration of formic acid in the original solution, calculated from the amount of the acid in the distillate, was almost identical with that found by potentiometric titration of the periodic acid solution before and after the oxidation of cellulose, so that it is evident that formic acid is the only other acidic product of the oxidation besides carbonic acid. The virtually quantitative separation of formic acid from mixtures containing periodic and iodic acid by the distillation process used was confirmed by control experiments with known amounts of formic acid, the recovery of formic acid was 97-98 per cent.

The identity of the acid produced was further confirmed by means of its lead salt. A periodic acid solution that had been used to oxidize cellulose was distilled in the way described above, and the distillate was neutralized with lead carbonate, filtered and evaporated until crystallization began. The salt was obtained in the form of needle-shaped crystals like those of lead formate, and estimation of lead by precipitation and weighing as lead chromate gave a lead content of 69.1 per cent, the calculated value for lead formate is 69.7 per cent. A metaperiodate solution that had been used in the oxidation of cellulose was similarly treated, except that it was acidified with phosphoric acid before distillation, and the salt isolated was found to have a lead content of 69.5 per cent.

By means of potentiometric titration of the oxidizing solution before and after its use in the oxidation of cellulose, the yield of formic acid was determined in a number of oxidations of cotton linters with periodic acid and metaperiodate. The results have been given in Table IV

#### Identification and Estimation of Formaldehyde Produced by Oxidation of Cellulose

It was found that solutions of periodic acid or metaperiodate that had been used to oxidize cellulose—or the distillates obtained from these solutions by the procedure described in connection with the separation of formic acid—when brought to a *pH* of about 6 gave a precipitate with a solution of dimedone (dimethylcyclohexanedione), a reagent for the detection of aldehydes (cf. Vorlander<sup>21</sup>). This precipitate, after recrystallization from ethyl alcohol, had a melting point of 190–191° C. (uncorrected), which was identical with that found for the condensation product of dimedone and formaldehyde. The production of formaldehyde during the oxidation process was thus established.

The dimedone derivative was also used in the estimation of the formaldehyde produced, the method employed being similar to those used by Fleury and Lange<sup>25</sup> and by Karrer and Pfähler<sup>26</sup>. The solution resulting from the oxidation of cellulose was distilled under reduced pressure at 30° C. as already described, the distillate brought to a *pH* of about 6 by the addition of alkali, and an excess of a 10 per cent alcoholic solution of dimedone added. After about 18 hours the precipitate was filtered in a fritted-glass filter-crucible (G4), washed with cold water, dried at 110° C., and weighed. Control experiments with known amounts of formaldehyde showed that the distillation process gave a recovery of 84–90 per cent, and it was therefore necessary to apply a correction to the results obtained. Attempts to estimate formaldehyde in the presence of periodate and iodate proved unsatisfactory, apparently on account of the destruction of the dimedone by the periodate.

The yields of formaldehyde found in oxidations of cotton linters by periodic acid and metaperiodate have been given in Table IV.

#### Action of Periodic Acid on Formaldehyde and Formic Acid

The action of periodic acid on formaldehyde and formic acid was investigated by mixing a measured volume of a standard solution of each of these substances with a measured volume of a standard solution of periodic acid, and following the change of the periodic acid concentration by titration of aliquot portions according to the procedure of Fleury and Lange<sup>15</sup> already mentioned. The results obtained are recorded in Table VIII.

Table VIII  
Action of Periodic Acid on Formaldehyde and Formic Acid

Time (hours)	Gram-atoms of oxygen consumed per mole of formaldehyde or formic acid		
	[H CHO] = 0.0255M [H <sub>5</sub> IO <sub>6</sub> ] = 0.0944M	[H CHO] = 0.0255M [H <sub>5</sub> IO <sub>6</sub> ] = 0.0472M	[H COOH] = 0.05M [H <sub>5</sub> IO <sub>6</sub> ] = 0.0944M
20	0.189	0.081	0.011
44	0.374	0.170	0.018
68	0.509	0.250	0.026
92	0.607	0.315	0.034
164	0.813	0.484	0.061
217	0.898	0.576	0.077
336	0.992	0.732	0.112
408	—	0.794	—
480	—	0.843	—

**Action of Iodic Acid on Cellulose**

Cotton (linters) was treated with 0.2M iodic acid at 20° C for various times and the fluidities of the products in cuprammonium solution determined. The results are given in Table IX.

**Table IX**  
**Action of Iodic Acid on Cotton**

Time of treatment (hours)	0	48	144	288
Fluidity in cuprammonium solution	5.6	6.9	8.3	9.2

Iodometric titration showed that the concentration of the iodic acid was not changed by the treatment of cellulose, so that the observed increases of fluidity must be ascribed to acid attack

**SUMMARY**

The oxidation of cellulose by periodic acid and metaperiodate has been studied over a range of oxygen consumption up to more than an atom per glucose unit.

The oxycelluloses obtained from cotton cellulose by the action of these oxidants are characterized by high fluidity in cuprammonium solution, great reducing power, ability to combine with bisulphite, and low affinity for Methylene Blue. On treatment with cold or hot dilute sodium hydroxide solution, or with hot water, they suffer losses of weight which attain great proportions at high degrees of oxidation. The tensile strength of cotton yarn falls on oxidation with periodic acid, but after the consumption of 0.7 atom of oxygen per glucose unit the yarn still retains 30 per cent of its original strength.

The oxidation of cellulose by periodic acid has been formulated by Jackson and Hudson as a reaction completed by the consumption of one oxygen atom per glucose unit, and involving no degradation of the cellulose to oxidation products of low molecular weight. This must be regarded as an ideal reaction to which the oxidation of cotton cellulose with periodic acid approximates, but it is accompanied or followed by other reactions. The actual oxidation gives rise to notable proportions of formaldehyde, formic acid, and carbon dioxide, and the loss of weight by the cellulose during oxidation is greater than that calculated on the basis of the ideal mechanism. By measurement of the nitrogen contents of nitrocelluloses derived from periodic acid oxycelluloses it has been found that these oxycelluloses contain a greater proportion of hydroxyl groups than corresponds to oxidation according to the ideal reaction. A comparison of results obtained with periodic acid and metaperiodate shows that although the oxidation with metaperiodate also diverges from the ideal course, the divergence is less than when periodic acid is the oxidant.

Progressive oxidation by periodic acid leads with filter paper to a marked contraction in area and increase in thickness, and with cotton yarn to a considerable contraction in length. It also results in broadening of the lines of the X-ray diagram of the cellulose, and yields oxycelluloses that are more hygroscopic than the unoxidized material. These effects suggest that the oxidation is not confined to the amorphous part of the cellulose, but that the crystalline regions are gradually opened up and attacked.

Nitrocelluloses derived from periodic acid oxycelluloses are incompletely soluble in acetone when the oxygen consumption in the preparation of the parent oxycellulose exceeds about one atom to fifty glucose units

Some of the experimental work was done by Miss E. H. Elding. The X-ray photographs were taken by Dr. M. O. Pelton

#### REFERENCES

- <sup>1</sup> Jackson and Hudson *J Amer Chem Soc*, 1937, 59, 2049
- <sup>2</sup> Jackson and Hudson *J Amer Chem Soc*, 1938, 60, 989
- <sup>3</sup> Davidson *Shirley Inst Mem*, 1939-40, 17, 83, or *J. Text Inst*, 1940, 31, 181
- <sup>4</sup> Birtwell, Clibbens and Ridge *Shirley Inst Mem*, 1924, 3, 321, or *J Text Inst*, 1925, 16, 113
- <sup>5</sup> Clibbens, Geake and Ridge *Shirley Inst Mem*, 1927, 6, 65, or *J Text Inst*, 1927, 18, 1277
- <sup>6</sup> Urquhart, Bostock and Eckersall *Shirley Inst Mem*, 1932, 11, 61, or *J Text Inst*, 1932, 23, 1135
- <sup>7</sup> Knecht and Thompson *J. Soc Dyers and Col*, 1922, 38, 132
- <sup>8</sup> Brissaud *Mém Poudres*, 1938, 28, 54
- <sup>9</sup> Davidson *Shirley Inst Mem*, 1937-38, 16, 29, or *J Text Inst*, 1938, 29, 1195
- <sup>10</sup> Caldwell and Hixon *J Biol Chem*, 1938, 123, 595
- <sup>11</sup> Staudinger and Daumiller *Liebigs Ann Chem*, 1937, 529, 219
- <sup>12</sup> Kraemer and Lansing *J Phys Chem*, 1935, 39, 153
- <sup>13</sup> Kraemer *Ind Eng Chem*, 1938, 30, 1200
- <sup>14</sup> Muller and Friedberger *Ber deut chem Ges*, 1902, 35, 2652
- <sup>15</sup> Fleury and Lange *J Pharm Chim*, 1933, 17, 107
- <sup>16</sup> Clibbens and Geake *Shirley Inst Mem*, 1927, 6, 117, or *J Text Inst*, 1928, 19, 177
- <sup>17</sup> Department of Scientific and Industrial Research Fabrics Co-ordinating Research Committee "The Viscosity of Cellulose Solutions," H M Stationery Office, London, 1932.
- <sup>18</sup> Clibbens and Little *Shirley Inst Mem*, 1936, 15, 25, or *J Text Inst*, 1936, 27, 1285
- <sup>19</sup> Clibbens and Geake *Shirley Inst Mem*, 1923, 2, 383, or *J Text Inst*, 1924, 15, 127
- <sup>20</sup> Birtwell, Clibbens and Ridge *Shirley Inst Mem*, 1923, 2, 227; or *J Text Inst*, 1923, 14, 1297
- <sup>21</sup> Clibbens and Geake *Shirley Inst Mem*, 1926, 5, 19, or *J Text Inst*, 1926, 17, 1127
- <sup>22</sup> Midgley and Peirce *Shirley Inst Mem*, 1926, 5, 77, or *J Text Inst*, 1926, 17, 1305
- <sup>23</sup> Reid and Weihe *Ind Eng Chem, Anal Ed*, 1938, 10, 271.
- <sup>24</sup> Vorländer *Z anal Chem*, 1929, 77, 241
- <sup>25</sup> Fleury and Lange *J Pharm Chim*, 1933, 17, 196.
- <sup>26</sup> Karrer and Pfaehler *Helv. Chim Acta*, 1931, 17, 766

## 10—THE PROGRESSIVE OXIDATION OF COTTON CELLULOSE BY CHROMIC ACID OVER A WIDE RANGE OF OXYGEN CONSUMPTION

By G F DAVIDSON

(The British Cotton Industry Research Association)

(Copyright by The Textile Institute)

### INTRODUCTION

Previous work in these laboratories has shown that the oxycelluloses formed in the very early stages of the oxidation of cotton cellulose by chromic acid (dichromate in the presence of sulphuric or oxalic acid) belong to the class of highly reducing, non-acidic, alkali-sensitive oxycelluloses<sup>1, 2, 3</sup> Since the products of the action of periodic acid on cotton are characteristic members of the same class,<sup>4</sup> a comparison of the two oxidation processes over a more extended range of oxidative attack is desirable. In the foregoing paper<sup>5</sup> the results of a study of the oxidation of cotton cellulose by periodic acid over a wide range of oxygen consumption have been reported, and the present paper describes an investigation, over a similar range and by similar methods, of the oxidation by chromic acid. The oxidation of cellulose by dichromate in the presence of oxalic acid has the disadvantage that, owing to simultaneous oxidation of oxalic acid, the consumption of oxygen by the cellulose cannot be readily determined, and the work to be described is confined to oxidation with dichromate in the presence of sulphuric acid. The oxidation of cellulose by chromic acid in 90 per cent acetic acid has been studied by Hibbert and Parsons<sup>6</sup> over a wide range of oxygen consumption, but their investigation was not sufficiently comprehensive to form the basis of the proposed comparison with periodic acid oxidation.

### DESCRIPTION OF RESULTS

#### Copper Number and Fluidity of Oxycelluloses; Loss of Weight by Oxycelluloses on Treatment with Dilute Alkali and Hot Water

Among the properties measured in the investigation of the periodic acid oxycelluloses<sup>5</sup> were the copper number, the fluidity in cuprammonium solution, and the loss of weight suffered by the oxycelluloses when they were treated under standardized conditions with cold and hot dilute sodium hydroxide solution and with hot water. Corresponding data have been collected for chromic acid oxycelluloses, and the relations between these properties and the oxygen consumption during the formation of the oxycelluloses are illustrated in Figs 1 and 2. It is seen that the values of all five properties increase with increasing oxygen consumption until the latter has attained a value of about 0.4 atom per glucose unit, and then remain almost constant as the degree of oxidation is further increased. This behaviour is in striking contrast to that observed with the periodic acid oxycelluloses, the corresponding properties of which are found to change continuously throughout the whole range of oxygen consumption investigated. In the early stages of oxidation the periodic acid oxycelluloses show higher values of these properties than chromic acid oxycelluloses of equal oxygen consumption, and the disparity becomes much greater in the later stages where the properties of the chromic acid oxycelluloses have become constant.

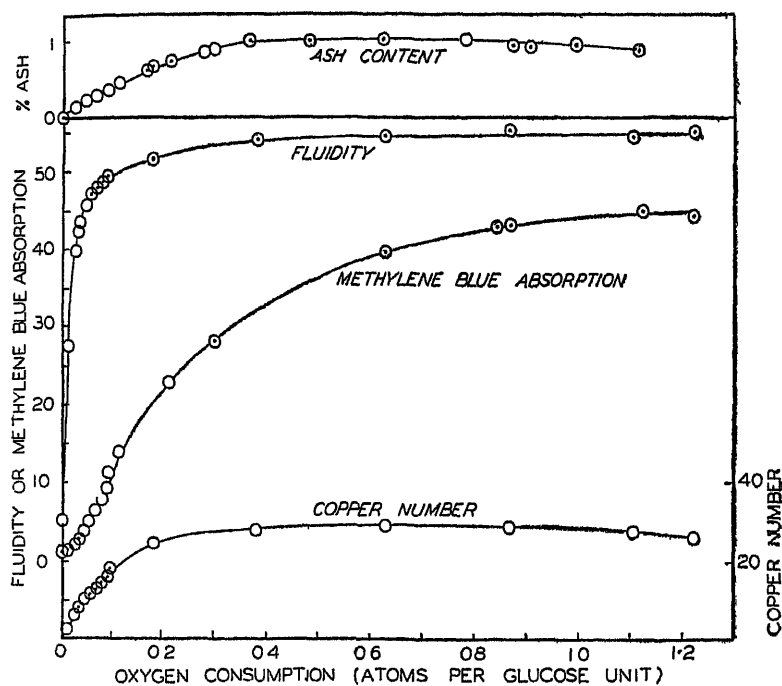


Fig. 1

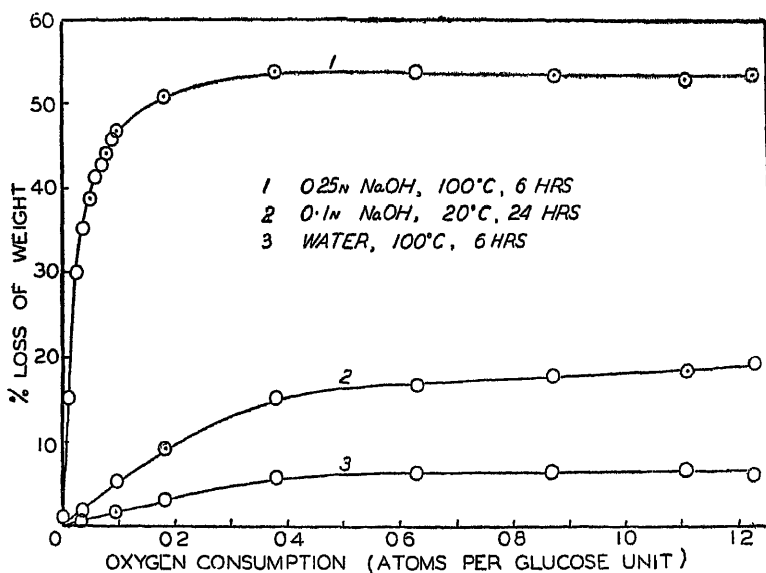


Fig. 2

#### Retention of Chromium by Oxycelluloses

Earlier work<sup>1</sup> has shown that oxycelluloses prepared by the action of dichromate in the presence of sulphuric acid contain trivalent chromium which cannot be removed by washing with dilute sulphuric acid. As the degree of oxidation of the cellulose is increased the presence of this chromium shows itself in the colour of the oxycellulose, which is blue-grey when the

oxycellulose is in the air-dry state, and green when it is dried over phosphorus pentoxide. A curve illustrating the variation of the ash content of the oxycelluloses with the oxygen consumption is included in Fig 1. It shows that the ash content, like the other properties already considered, increases with increasing degree of oxidation and then becomes approximately constant when the oxygen consumption exceeds about 0.4 atom per glucose unit. The ash consists mainly of chromic oxide, but in most cases extraction of the ash with hot water gives a pale yellow solution which shows the reactions of chromate. It seems probable that this chromate is produced during the ashing, for it is known (cf Britton<sup>7</sup>) that when chromium is precipitated as hydroxide and the precipitate ignited, the chromic oxide usually contains appreciable amounts of chromate. The formation of chromate in this way apparently requires the presence of alkali, and it is suggested that in the case of the oxycelluloses the necessary alkali is combined with the oxycellulose in the manner characteristic of the acidic oxycelluloses (e.g., alkaline hypobromite oxycelluloses), which give an alkaline ash even after being washed with acid.<sup>8</sup> Although the retained chromium is not removed by washing with dilute sulphuric acid, it may be partially removed by extraction of the oxycellulose with oxalic acid solution, for example, an ash content of 0.38 per cent was reduced to 0.12 per cent by shaking the oxycellulose with  $N/2$  oxalic acid for 24 hours.

#### Absorption of Methylene Blue by Oxycelluloses

Previous work in these laboratories has indicated that the absorption of Methylene Blue by cotton cellulose is not much affected by slight oxidation of the cellulose with chromic acid.<sup>1</sup> The present work shows, however, that this is true only within a very restricted range of oxidative attack, and that, as suggested by the qualitative observations of Hibbert and Parsons<sup>6</sup>, highly-oxidized products display a very much enhanced affinity for Methylene Blue (Fig 1). The behaviour of the chromic acid oxycelluloses in this respect is thus very different from that of the periodic acid oxycelluloses, which even at high degrees of oxidation show an absorption little greater than that of the unoxidized cotton. Fig 1 shows that the absorption by chromic acid oxycelluloses, unlike the other properties already dealt with, does not become constant at an oxygen consumption of 0.4 atom per glucose unit. The rate of increase of the absorption becomes very small at oxygen consumptions in the neighbourhood of one atom per glucose unit, but under the experimental conditions employed the dye solution is nearly exhausted by materials of this degree of oxidation. The high Methylene Blue absorption displayed by the chromic acid oxycelluloses does not appear to be closely connected with the high ash content, for when the latter was reduced to about a third of its original value by extraction with oxalic acid solution, the Methylene Blue absorption was found to be slightly increased, for example, reduction of the ash content from 0.38 per cent to 0.12 per cent was accompanied by a rise in the Methylene Blue absorption from 9.7 to 10.0.

Neale<sup>9,10</sup> has shown that oxycelluloses, such as the alkaline hypobromite oxycelluloses, which display an enhanced affinity for Methylene Blue, are able to liberate acid from solutions of neutral salts, such as sodium chloride. The highly modified products of the action of chromic acid also possess this power, and the oxycellulose, after treatment with salt solution and washing with water, shows a higher ash content and yields an ash containing a considerably greater proportion of chromate than before.

### Action of Bisulphite on Oxycelluloses

Chromic acid oxycelluloses combine with sodium bisulphite, as is shown by the fact that the well-washed products of the action of bisulphite on the oxycelluloses yield sulphur dioxide on heating with dilute sulphuric acid. The proportion of bisulphite bound is, however, much smaller than with periodic acid oxycelluloses. When the proportion of oxygen consumed in the preparation of the chromic acid oxycellulose is less than 0.3 atom per glucose unit the treatment with bisulphite leads to a slight increase of weight, but at higher degrees of oxidation there is a slight loss of weight. The treatment results in the removal of part of the chromium in the oxycellulose, but the loss of weight that occurs with the more highly oxidized materials is probably due mainly to the dissolution of a portion of the oxycellulose in the bisulphite solution

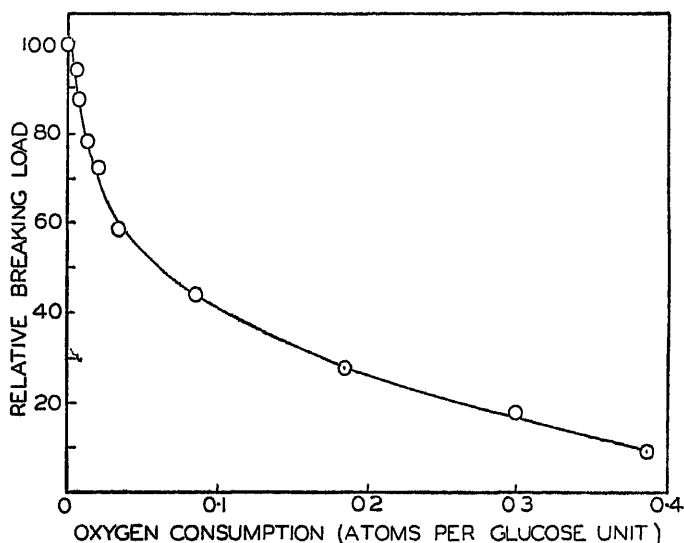


Fig. 3

### Tensile Strength of Oxidized Yarn

Cotton oxidized with chromic acid falls to a powder when the oxygen consumption reaches about 0.4 atom per glucose unit. A quantitative investigation of the relation between oxygen consumption and tensile strength has been made with a cotton yarn, and the results are shown graphically in Fig. 3. The relation is almost identical with that found for periodic acid oxidation up to an oxygen consumption of 0.05 atom per glucose unit, but further oxidation leads to a much more rapid fall of strength with chromic acid than with periodic acid. Whereas at an oxygen consumption of 0.4 atom per glucose unit the yarn oxidized with chromic acid has lost 92 per cent of its original strength, the corresponding loss as a result of periodic acid oxidation is only 66 per cent.

### Dimensional Changes during Oxidation of Cellulose: Effect of Oxidation on X-ray Diagram

One of the most striking effects produced by the oxidation of cellulose with periodic acid is the very marked swelling that accompanies it. With filter paper this swelling shows itself in a contraction in area and an increase



in thickness, whilst with cotton yarn the most obvious manifestation is a marked longitudinal shrinkage. Oxidation with chromic acid, on the other hand, is found to produce no important change in the length of a cotton yarn, and in this respect it resembles the action of hydrochloric acid. A further difference between the actions of the two oxidants which is probably connected with the difference in regard to swelling is that, whereas periodic acid oxidation renders the lines in the X-ray diagram of cellulose more diffuse, oxidation with chromic acid has no effect on the diagram.

#### Hygroscopicity of Oxycelluloses

It was found that periodic acid oxycelluloses were more hygroscopic than the parent cotton, and that the hygroscopicity increased continuously with increasing degree of oxidation. Similar measurements of moisture absorption were made with chromic acid oxycelluloses, and the results obtained are given in Table I. They are expressed in terms of the moisture absorption ratio, which is the ratio of the amount of moisture absorbed by the oxycellulose to that absorbed by the unoxidized cotton under the same conditions.

Table I  
Moisture Absorption of Chromic Acid Oxycelluloses

Oxygen consumption (atoms per glucose unit)	0	0.0101	0.0342	0.0567	0.0785	0.097	0.182	0.381	0.631	0.868
Moisture absorption ratio	1.00	1.06	1.08	1.11	1.14	1.16	1.19	1.19	1.23	1.22

The Table shows that the moisture absorption ratio increases in the early stages of oxidation, but becomes approximately constant at a value of 1.2 when the oxygen consumption exceeds about 0.2 atom per glucose unit. The highest value of the ratio attained as a result of periodic oxidation was 1.8, so that here also there is a marked difference between the two types of oxycellulose.

It is possible that the enhanced hygroscopicity of the chromic acid oxycelluloses is due, wholly or in part, to the chromium compound they contain, and support for this hypothesis is provided by the observation that when the ash content is reduced to about a third of its original value by extraction of the oxycellulose with oxalic acid solution, there is a significant diminution of the moisture absorption ratio of the oxycellulose (Table II).

Table II  
Effect of Partial Removal of Chromium on the Moisture Absorption of Chromic Acid Oxycelluloses

Oxygen consumption (atoms per glucose unit)	% Ash		Moisture absorption ratio	
	Original oxycellulose	After extraction with oxalic acid	Original oxycellulose	After extraction with oxalic acid
0.087	0.40	0.14	1.15	1.08
0.137	0.59	0.19	1.15	1.10
0.290	0.90	0.29	1.18	1.08

#### Properties of Nitrocelluloses Derived from Oxycelluloses

In order to obtain information regarding the proportion of the hydroxyl groups in cellulose that is destroyed during oxidation with chromic acid, oxycelluloses were nitrated by a procedure that effects almost complete

esterification of an unmodified cotton and the nitrogen contents of the nitrocelluloses were determined. The results obtained are given in Table III. As the degree of oxidation increases the nitrogen content of the nitrocellulose derived from the oxycellulose falls gradually to about 13.2 per cent., a value that is reached at an oxygen consumption of about 0.5 atom per glucose unit, and thereafter remains almost constant.

**Table III**  
**Nitrogen Content and Fluidity in Acetone Solution of Nitrocelluloses Derived from Oxycelluloses**

Oxygen consumption in preparation of oxycellulose (atoms per glucose unit)					
0	0.182	0.381	0.631	0.868	1.106
Nitrogen content of derived nitrocellulose, %					
13.73	13.49	13.30	13.19	13.17	13.20
Fluidity of derived nitrocellulose (0.25% solution)					
3.6	118.4	139.4	175.0	190.8	—

With nitrocelluloses derived from periodic acid oxycelluloses, on the other hand, the nitrogen content was found to decrease continuously with increasing degree of oxidation, the value corresponding to an oxygen consumption of one atom per glucose unit being about 10 per cent. Nitration of an unmodified cotton to a nitrogen content of 13.2 per cent would correspond to the esterification of some 90 per cent. of the hydroxyl groups, so that the results obtained with the chromic acid oxycelluloses may be regarded as an indication that the oxidized products resulting from the consumption of more than 0.5 atom of oxygen per glucose unit still retain about 90 per cent. of the hydroxyl groups present in the unoxidized cellulose.

The nitrocelluloses prepared from periodic acid oxycelluloses were found to be incompletely soluble in acetone when the oxygen consumption was greater than about 0.02 atom per glucose unit, but dissolution of those derived from chromic acid oxycelluloses is substantially complete at all degrees of oxidation. Table III includes data for the fluidity of 0.25 per cent. solutions of the nitrocelluloses examined. It is found that, at a given cuprammonium fluidity of the parent modified cotton, the nitrocellulose derived from a chromic acid oxycellulose has a lower fluidity than that derived from a hydrocellulose, and this is to be expected in view of the alkali-sensitive character of the chromic acid oxycelluloses.<sup>3</sup>

#### Soluble Products of the Oxidation

The constancy of the properties of the chromic acid oxycelluloses beyond an oxygen consumption of about 0.4 atom per glucose unit suggested that oxygen was being consumed in the formation of soluble products during the later stages of the oxidation. Preliminary experiments confirmed the statement of Hibbert and Parsons<sup>6</sup> that carbon dioxide is produced, and showed that the solutions that have been used to oxidize cellulose contain material capable of being further oxidized. A systematic study was therefore made in which the carbon dioxide yield, the loss of weight suffered by the cellulose during oxidation, the ash content of the oxycellulose, and the amount of oxygen necessary for the complete oxidation of the soluble products were all measured. The latter quantity was determined by the method of wet combustion as used in the estimation of cellulose, and the amount of oxygen consumed in this oxidation was expressed as a percentage of the weight of cotton from which the soluble, oxidizable material was produced.

The relations between the proportion of oxygen consumed by the cellulose and the carbon dioxide yield, the loss of weight (corrected for ash content), and the amount of oxygen required for the oxidation of the soluble products are illustrated in Fig. 4. It is seen that in the early stages of the oxidation the amount of carbon dioxide produced is extremely small, but that beyond an oxygen consumption of 0.2 atom per glucose unit the amount formed increases rapidly. The formation of soluble oxidizable products is appreciable from the beginning of oxidation, but its rate increases at about the point where the carbon dioxide yield becomes measurable, and then falls off again above an oxygen consumption of 0.6 atom per glucose unit. The slope of the curve relating loss of weight and oxygen consumption also increases in the early stages of the oxidation and finally becomes almost constant.

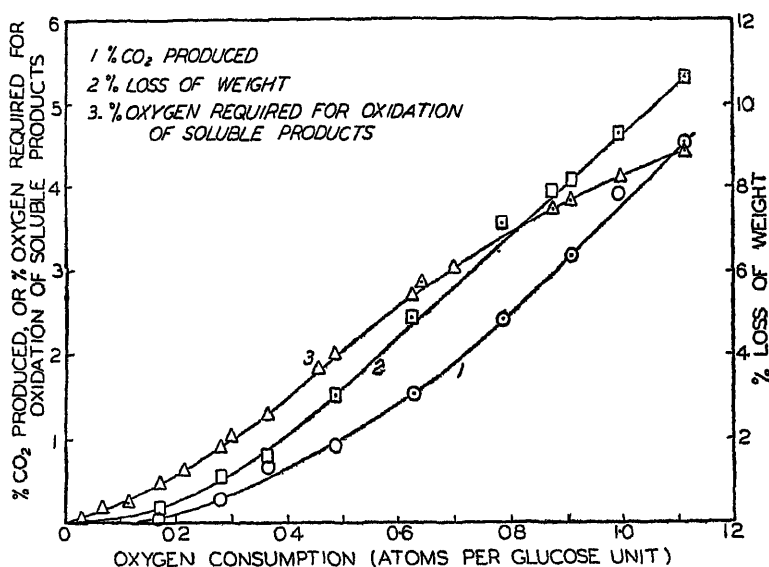


Fig. 4

At this stage an oxygen consumption of 1 per cent leads to a loss of weight of 1.2 per cent, whereas the consumption of the same proportion of oxygen in the complete oxidation of a portion of the cellulose to carbon dioxide and water would correspond to a loss of 0.84 per cent. The high rate of loss of weight in the later stages of the oxidation of cellulose is evidently due to the fact that the soluble products contain, in addition to carbon dioxide, a considerable proportion of material capable of being further oxidized.

It has been shown that formic acid and formaldehyde are produced during the oxidation of cellulose by periodic acid, and a search for these substances in chromic acid solutions that had been used to oxidize cellulose was therefore made. The solution, after partial neutralization with sodium hydroxide, was distilled under reduced pressure at 30° C. An acid found in the distillate was identified as formic acid by means of the lead content of its lead salt and by means of a determination of its dissociation constant by potentiometric titration with the glass electrode. The proportion of formic acid found was considerably smaller than in the periodic acid oxidation, the maximum being about 0.07 molecule per glucose unit at an oxygen consumption of 1.2 atoms per glucose unit. This proportion is quite

insufficient to account for the amount of oxygen required for the complete oxidation of the soluble oxidizable products. Formaldehyde could not be detected in the distillates by the very sensitive dimedone test. Even if it were formed it could have only a transient existence, for experiment showed that it is rapidly oxidized by chromic acid under the conditions employed in the oxidation of cellulose. Under these conditions the oxidation of formic acid was found to be relatively slow.

It is evident that the consumption of oxygen which occurs when cellulose is treated with chromic acid solution may be partly due to the further oxidation of soluble oxidation products from the cellulose. Some information regarding the part played by this process may be obtained from experiments in which, after the oxidation of the cotton has proceeded for some time, the oxycellulose is separated from the solution by filtration, the solution is main-

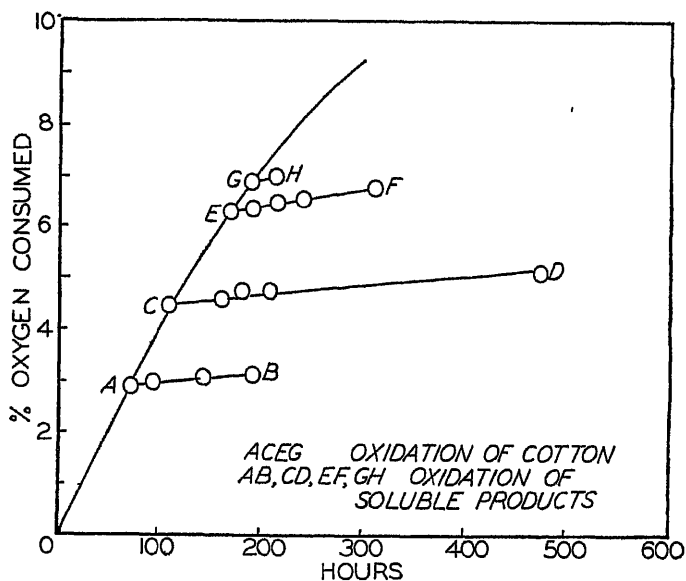


Fig. 5

tained at the temperature of oxidation and the concentration of chromic acid determined at intervals. The results obtained in experiments of this kind are illustrated in Fig. 5, in which the line ACEG represents the rate of oxygen consumption when 1 gram of cotton is treated with 100 c.c. of 0.2N chromic acid at 20°C, and the lines AB, CD, EF and GH represent the rates of oxygen consumption after the oxycellulose has been removed from the solution at times corresponding to the abscissae of the points A, C, E and G respectively, in all cases the oxygen consumption is expressed as a percentage of the weight of cotton initially present. From Fig. 5 it is evident that the further oxidation of the soluble products from the oxidation of the cellulose accounts for only a small part of the total oxygen consumption in the system.

#### Properties of Oxycelluloses Prepared from Mercerized Cotton

When mercerized cotton was employed as starting material in the preparation of chromic acid oxycelluloses it was found that the variation of the properties of the oxycelluloses with the oxygen consumption (Fig. 6) was

qualitatively similar to that observed when unmercerized cotton was used. The values of the properties corresponding to a given oxygen consumption were, however, uniformly higher with the mercerized than with the unmercerized material.

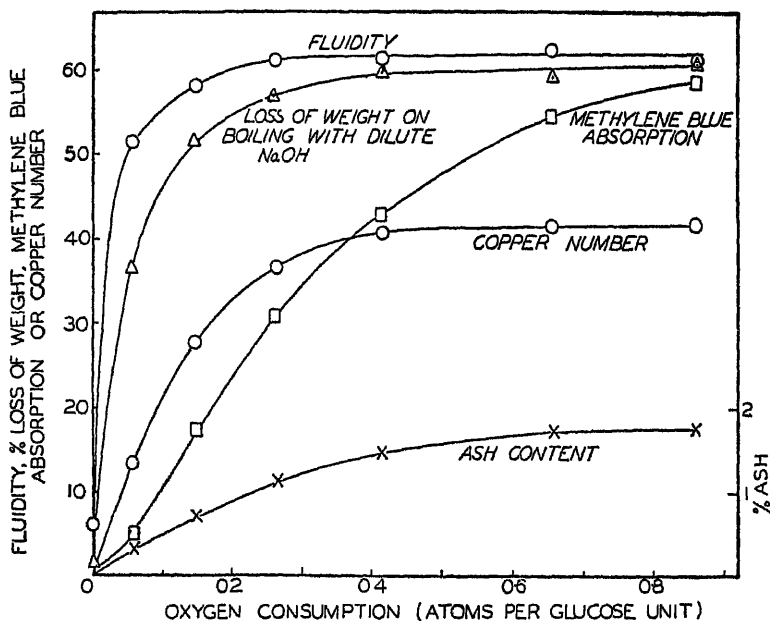


Fig. 6

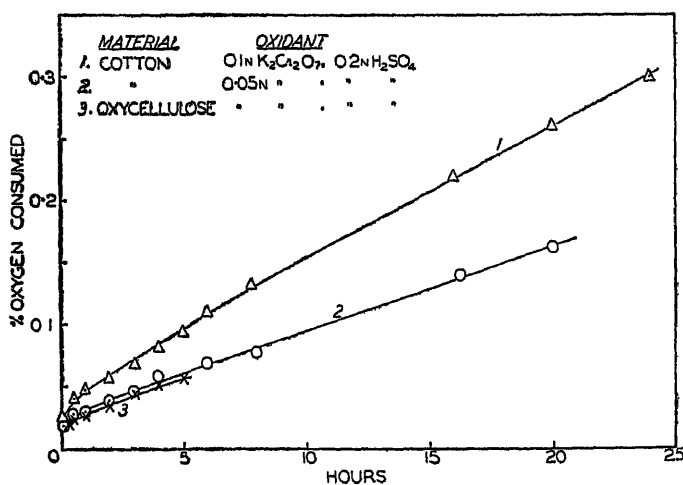


Fig. 7

#### Adsorption of Chromic Acid by Cellulose

An examination of the rate of oxidation of cotton by chromic acid more detailed than that incidental to the preparation of the required oxycelluloses showed that the consumption of oxygen, as measured by the fall of the chromic acid concentration, was relatively rapid during the first five minutes, the rate falling to an approximately constant value that was maintained for

many hours. This is illustrated by Curves 1 and 2 of Fig. 7, which relate to the oxidation of cotton by 0.1N and 0.05N chromic acid, respectively. Two possible explanations of the initial high rate of oxygen consumption suggested themselves, it might be due to the rapid oxidation of non-cellulosic material in the cotton, or to preferential adsorption of the oxidant by the cellulose. In order to decide between these two possibilities, cotton was treated for 16 hours with 0.05N chromic acid so as to oxidize any oxidizable non-cellulosic material that might be present, and the rate of oxidation of the resulting oxycellulose by 0.05N chromic acid was compared with that of the untreated cotton. Curve 3 of Fig. 7 illustrates the rate of consumption of oxygen by the pre-treated cotton, and it is evident that the form of the curve has not been affected by the preliminary oxidation. It thus appears probable that the initial rapid fall of concentration when cellulose is treated with chromic acid is due to adsorption. In calculating the consumption of oxygen in the preparation of oxycelluloses it has been assumed that the fall of the chromic acid concentration is due entirely to reduction by the cellulose, but if the fall is partly due to adsorption the calculated oxygen consumptions must be too high. The error due to this cause will be the less important the higher the oxygen consumption.

The adsorption by cellulose of another oxidizing agent, hypochlorite, has been demonstrated by Seck<sup>11</sup>

#### DISCUSSION

Although the oxycelluloses formed in the very early stages of the oxidation of cellulose by chromic acid show many points of resemblance to those prepared by periodic acid oxidation, the results presented in this and the preceding paper reveal profound differences between the actions of the two oxidants. The observed differences seem to indicate that cellulose is attacked in a more uniform manner by periodic acid than by chromic acid, the latter having access to only a portion of the cellulose and leaving the remainder unattacked. That these portions not accessible to chromic acid oxidation are the crystalline regions of the cellulose is suggested by the X-ray results, which show that the crystalline structure is not destroyed by a high degree of oxidation with chromic acid. The X-ray diagrams of periodic acid oxycelluloses, on the other hand, indicate the gradual destruction of the crystalline order as the oxidation proceeds. The pronounced swelling and increase of hygroscopicity that accompany periodic acid oxidation and the negligible dimensional changes and limited increase of hygroscopicity that result from chromic acid oxidation are consistent with this interpretation.

On the basis of these views the following picture of the oxidation of cellulose by chromic acid may be given. In the early stages those parts of the chain-molecules that lie within the inter-crystalline regions are oxidized at points along their length and are either broken or rendered susceptible to rupture by the action of alkalis, properties such as copper number, loss of weight under the action of alkalis, and fluidity in cuprammonium solution increase with increasing oxygen consumption, but there is little loss of weight due to the formation of soluble products. As the oxidation proceeds, however, the production of carbon dioxide and other soluble substances assumes greater prominence, until finally a stage is reached in which the greater part of the oxygen consumed is used in the formation of soluble products, leaving only a small fraction of the oxygen consumption

to effect further modification of the properties of the insoluble residue. In this stage the net effect of the elimination of the most highly oxidized portions as soluble products and the further oxidation of the remainder is to leave the properties of the resulting oxycellulose almost constant. The Methylene Blue absorption is the only property among those studied that does not attain a constant value, and this must be attributed to the progressive formation of acidic groups. Although it has been suggested that the crystalline regions in cellulose are not attacked by chromic acid, this does not mean that a part of the oxycellulose retains the properties of unmodified cellulose. The chain-molecules forming a crystalline region will initially extend through the surrounding amorphous regions and take part in the structure of other crystalline regions, but after oxidation in the manner suggested they will tend to be conterminous with the crystalline region and thus to have a considerably lower average chain-length than the chain-molecules of the original cellulose.

Little is known regarding the chemical reactions underlying the action of chromic acid on cellulose, and the contribution to knowledge of these reactions made by the present investigation is limited to the demonstration that oxidation with chromic acid does not follow the same course as oxidation with periodic acid. Staudinger and Sohn<sup>12</sup> have suggested a mechanism for the oxidation of cellulose by chromic acid that involves the conversion of glycosidic linkages to carbonic ester linkages, but the only reason advanced for the proposed reaction is that it would explain why the chain-molecules of chromic acid oxycelluloses are readily broken by alkalis. The same reason, however, could be given for assigning such a mechanism to the oxidation of cellulose by periodic acid, which produces oxycelluloses that are even more alkali-sensitive than the chromic acid oxycelluloses.<sup>4</sup>

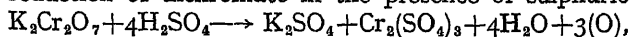
## EXPERIMENTAL

### Materials

Except where otherwise stated, the starting material in the oxidations was the sample of cotton linters used in the investigation of periodic acid oxidation.<sup>5</sup> The yarn employed in the study of the changes in length and tensile strength produced by chromic acid oxidation was that employed in the corresponding work with periodic acid<sup>5</sup>, and the material referred to as mercerized cotton was a product obtained from the cotton linters by treatment with 25 per cent. sodium hydroxide solution.

### Methods of Oxidation

Oxidation by chromic acid was effected by treating the cotton at 20° C with solutions of potassium dichromate containing sulphuric acid, the oxygen consumption during the oxidation being calculated from the change in the concentration of the oxidizing solution. The equation which represents the reduction of dichromate in the presence of sulphuric acid, viz ,



indicates that 1 equivalent of dichromate requires  $1\frac{1}{2}$  equivalents of sulphuric acid, the proportions actually employed were 2 equivalents of sulphuric acid to 1 equivalent of dichromate. In order to obtain a series of oxycelluloses covering a wide range of oxygen consumption, cotton was treated for various times with a solution 0.2N with respect to dichromate and 0.4N with respect to sulphuric acid, the ratio of cotton to solution being 1 gram per 100 c c. These conditions permit of a maximum oxygen consumption of

16 per cent, or about 1.6 atoms per glucose unit. They are not, however, very suitable for the preparation of oxycelluloses of low degree of modification, since the change of concentration is then too small to be accurately measured. On this account the oxycelluloses prepared as above were supplemented by others in the preparation of which the dichromate concentration was reduced to 0.1N and the ratio of cotton to solution increased to 2 grams per 100 c.c. The concentration changes were measured by titration of the dichromate solutions with standard ferrous ammonium sulphate solutions, phenylanthranilic acid being used as indicator.

Sulphuric acid of the concentrations employed in the oxidizing solutions exerts very little hydrolytic action on cellulose under the conditions of temperature and time of treatment used in the oxidations; this is shown in Table IV, which gives the cuprammonium fluidities of the cotton after various times of treatment with 0.4N sulphuric acid at 20° C.

Table IV  
Effect of 0.4N Sulphuric Acid on Cotton at 20° C.

Time of treatment (hours)	0	24	48	95	168	240	336	432
Fluidity	5.6	6.7	7.1	7.7	8.6	9.2	9.9	10.4

#### Properties of Oxycelluloses

*Copper number, fluidity in cuprammonium solution, and loss of weight on treatment with cold and hot sodium hydroxide solution and with hot water.* These properties were measured in the same way as those of the periodic acid oxycelluloses<sup>5</sup>. The results obtained are given in Table V and illustrated in Figs. 1 and 2.

*Ash content.* The oxycelluloses were compressed into cylindrical tablets by means of a press, dried at 110° C, weighed and ashed in a porcelain crucible. The results are given in Tables V and IX, and the variation of the ash content with the oxygen consumption is shown graphically in Fig. 1.

*Methylene Blue absorption.* The procedure adopted for the determination of the Methylene Blue absorption was essentially the same as that used with the periodic acid oxycelluloses<sup>5</sup>, but, in order to facilitate the attainment of equilibrium when the oxycellulose was in the form of a powder, the mixture of dye solution and oxycellulose was agitated instead of being allowed to stand. The oxycellulose and the Methylene Blue solution were contained in a stoppered centrifuge bottle which was attached to a revolving wheel, and after 18 hours the oxycellulose was centrifuged down and an aliquot portion of the solution pipetted out for analysis. In order to cover the wide range of absorptive capacity that was found to exist it was necessary to reduce the ratio of oxycellulose to dye solution as the degree of oxidation increased. With the most highly oxidized products 0.25 g. was used with 30 c.c. of solution, and even with this low ratio the solution was nearly exhausted in some cases.

The absorptions that have been measured are given in Table VI, and it is seen that where measurements were made on the same material with two different ratios of oxycellulose to solution the lower ratio gives the higher absorption. This is in accordance with expectation, since the lower the ratio, the higher is the end-concentration of Methylene Blue.



Table V  
Properties of Oxycelluloses

Conditions of oxidation			Oxygen consumption (atoms per glucose unit)	Fluidity in cuprammonium solution	Copper number	% Loss of weight on treatment with			% Ash
	Temperature	Time (hours)				Water at 100° C for 6 hours	0.1N NaOH at 20° C. for 24 hours	0.25N NaOH at 20° C. for 6 hours	
0.1N $K_2Cr_2O_7$ , 0.2N $H_2SO_4$ , 2 g Cotton per 100 c c	20° C.	0	0	5.6	0.14	—	—	1.0	0.036
	"	5.5	0.0101	27.5	2.41	—	—	15.2	0.077
	"	18	0.0239	39.8	6.03	—	—	29.8	0.154
	"	28.5	0.0342	43.5	8.01	—	—	35.3	0.187
	"	41	0.0473	45.7	10.2	—	—	38.9	0.228
	"	54	0.0567	47.0	11.6	—	—	41.5	0.264
	"	66	0.0682	47.8	13.1	—	—	42.9	0.295
	"	78	0.0785	48.4	14.6	—	—	44.2	0.334
	"	94	0.0902	49.2	16.2	—	—	45.9	0.362
	"	8	0.032	42.2	8.9	0.5	1.7	35.6	—
0.2N $K_2Cr_2O_7$ , 0.4N $H_2SO_4$ , 1 g Cotton per 100 c c	"	24	0.097	49.5	18.5	1.6	5.4	46.7	—
	"	45	0.182	51.4	24.9	3.1	9.4	50.8	0.66
	"	96	0.381	53.7	28.1	5.7	15.4	53.8	—
	"	168	0.631	54.1	29.1	6.3	17.0	53.7	—
	"	259	0.868	55.0	28.5	6.7	17.9	53.4	—
	Room	379	1.106	54.1	27.5	6.6	18.4	52.8	—
	"	474	1.223	55.0	28.0	6.2	19.5	53.4	0.97
	"								
	"								
	"								

Table VI  
Absorption of Methylene Blue by Oxycelluloses

Oxygen consumption (atoms per glucose unit).	Absorption (m moles/100 g )			Oxygen consumption (atoms per glucose unit)	Absorption (m moles/100 g )	
	Wt of oxycellulose per 15 c c of solution.				Wt. of oxycellulose per 15 c c of solution.	
	1 g.	0.25 g	0.125 g		0.25 g	0.125 g
0	1 18	1.2	—	0 0902	8.7	9.1
0.0101	1.25	1.35	—	0 097	9.85	11.2
0 0239	1 81	2.0	—	0.0974	9.7	—
0.028	—	2.25	—	0.113	12.8	13.8
0.032	—	2.75	—	0.212	20.5	22.8
0 0342	2 51	2.65	—	0 299	22.9	28.0
0 0473	3.35	3.9	—	0 631	—	39.3
0 0567	4.12	5.1	—	0 845	—	42.8
0.0682	—	6.1	6.4	0.868	—	43.0
0.071	—	7.2	7.8	1.127	—	44.8
0 0785	—	7.2	7.7	1.223	—	44.2

The relation between Methylene Blue absorption and degree of oxidation is illustrated in Fig. 1.

*Change of weight on treatment with bisulphite.* The change of weight on treatment of chromic acid oxycelluloses with bisulphite was determined according to the procedure employed with periodic acid oxycelluloses<sup>5</sup>. The results obtained are given in Table VII.

Table VII  
Change of Weight on Treatment of Oxycelluloses with Bisulphite

Oxygen consumption (atoms per glucose unit) ...	0.063	0.140	0.217	0.313	0.570
Change of weight of oxycellulose, per cent	+1.0	+1.6	+1.2	+0.2	-0.9

*Hygroscopicity* The hygroscopicities of cotton and oxycelluloses derived from it were compared at 70 per cent. relative humidity by the method previously described<sup>5</sup>. The results have been given in Table I.

#### Tensile Strength of Oxidised Yarns

The effect of chromic acid oxidation on the tensile strength of cotton yarn was studied by the same method as was used with periodic acid.<sup>5</sup> The relation between oxygen consumption and tensile strength is shown in Table VIII and Fig. 3

Table VIII  
Relation between Oxygen Consumption and Tensile Strength

Oxygen consumption (atoms per glucose unit)	0	0.0045	0.0077	0.0127	0.0203	0.0340	0.085	0.185	0.299	0.386	0.489
Relative breaking load	100	94.7	87.5	78.5	72.7	58.9	44.3	28.4	18.0	9.1	*

\* Yarn too weak to measure breaking load.

#### Dimensional Changes during Oxidation of Yarn

The changes in the length of cotton yarn during oxidation with chromic acid were measured in the way previously described<sup>5</sup>. During oxidation with 0.2N dichromate, 0.4N with respect to sulphuric acid, there was a very slight extension of the yarn, the maximum extension under a load of 0.4 gram being 0.3 per cent.

**Preparation and Properties of Nitrocelluloses Derived from Oxycelluloses**

Nitrocelluloses were prepared from chromic acid oxycelluloses, and their nitrogen contents and fluidities in acetone solution were determined, by methods described in a previous paper.<sup>3</sup> The nitrogen contents and fluidities of the nitrocelluloses in relation to the oxygen consumption in the preparation of the parent oxycelluloses have been given in Table III

**Soluble Products of the Oxidation**

The loss of weight suffered by the cellulose and the yield of carbon dioxide during oxidation with chromic acid were determined as in the corresponding work with periodic acid.<sup>5</sup> The amount of oxygen required for the complete oxidation of the soluble products was measured in the following way. Ten c.c. of the solution that had been used to oxidize cellulose were mixed with 20 c.c. of water and 10 c.c. of concentrated sulphuric acid, and the mixture was boiled under reflux for an hour, the solution was then titrated with standard ferrous ammonium sulphate. In calculating the amount of oxygen consumed by the soluble products, a correction was applied for the very small loss of available oxygen that was found to occur when dichromate was heated with sulphuric acid under the conditions of the wet combustion.

The data relating to the soluble products of the oxidation of cellulose by chromic acid are given in Table IX and illustrated in Fig. 4

Formic acid was identified in the distillate from solutions that had been used to oxidize cotton by means of its dissociation constant and the lead content of its lead salt. The *pK* value found was 3.77, as against 3.84 for an authentic specimen of formic acid. The lead content of the salt of the acid in the distillate was 69.8 per cent, the calculated value for lead formate being 69.7 per cent.

**Table IX**  
**Soluble Products of Oxidation of Cellulose**

%	Oxygen consumption	Change of weight of cellulose on oxidation, %	Carbon dioxide produced %	Oxygen required for complete oxidation of soluble products, %	Ash in oxycellulose %	Loss of weight corrected for ash content %
	Atoms per glucose unit					
0.28	0.028	—	—	0.06	0.15	—
0.70	0.071	—	—	0.17	0.33	—
1.12	0.113	—	—	0.26	0.47	—
1.66	0.168	+0.27	0.04	0.47	0.65	0.38
2.09	0.212	—	—	0.62	0.72	—
2.76	0.280	-0.27	0.28	0.92	0.83	1.10
2.95	0.299	—	—	1.06	0.87	—
3.60	0.365	-0.62	0.66	1.30	0.99	1.60
4.49	0.455	—	—	1.85	—	—
4.79	0.485	-2.14	0.93	2.01	0.97	3.09
6.15	0.623	-3.90	1.66	2.70	1.01	4.87
6.31	0.639	—	—	2.87	—	—
6.91	0.700	—	—	3.04	—	—
7.75	0.785	-6.19	2.41	—	1.02	7.15
8.65	0.876	-7.05	—	3.73	0.93	7.91
8.97	0.909	-7.28	3.18	3.84	0.92	8.14
9.80	0.993	-8.40	3.92	4.11	0.96	9.28
11.02	1.117	-9.80	4.50	4.42	0.88	10.59

**Action of Chromic Acid on Formaldehyde and Formic Acid**

The rate of oxidation of formaldehyde and formic acid by chromic acid under the conditions used in the oxidation of cellulose was studied by mixing solutions of formaldehyde and formic acid of known concentration with an equal volume of a standard solution of chromic acid, and following the change of chromic acid concentration by titration of aliquot portions with standard ferrous ammonium sulphate solution. The results are given in Tables X and XI.

**Table X**  
**Action of Chromic Acid on Formaldehyde at 20° C.**

Initial concentrations — dichromate, 0.2N, sulphuric acid, 0.4M, formaldehyde, 0.0255M								
Time (hours)	0.5	1.25	2.25	4.25	5.75	24	48	
Gram-atoms of oxygen consumed per mole of formaldehyde	0.395	0.625	0.810	0.979	1.028	1.130	1.160	

**Table XI**  
**Action of Chromic Acid on Formic Acid at 20° C.**

Initial concentrations — dichromate, 0.2N, sulphuric acid, 0.4N, formic acid, 0.05M											
Time (hours)	5	24	48	72	96	120	168	218	264		
Gram-atoms of oxygen consumed per mole of formic acid	0.012	0.044	0.093	0.133	0.166	0.202	0.256	0.307	0.350		

**Properties of Oxycelluloses Prepared from Mercerized Cotton**

Oxycelluloses were prepared from mercerized cotton, and their properties measured, by the methods already described. The relations between the oxygen consumption and the various properties are shown in Table XII and Fig. 6

**Table XII**  
**Properties of Oxycelluloses Prepared from Mercerised Cotton**

One gram of mercerized cotton oxidized at 20° C with 100 c.c. of 0.2N dichromate, 0.4N in sulphuric acid

Time of oxidation (hours)	Oxygen consumption (atoms per glucose unit)	Fluidity in cupram- monium solution	Copper number	Loss of weight on treatment with 0.25N NaOH at 100° C for 6 hours, %	Ash, %	Methylene Blue absorption		
						Weight of oxy- cellulose per 15 c.c. of solution		
						1 g	0.125 g	0.0625 g
0	0	6.3	0.13	1.3	0.02	1.12	—	—
5	0.058	51.6	13.5	36.6	0.32	—	4.5	5.2
16	0.148	58.1	27.8	51.4	0.72	—	15.55	17.3
31	0.262	61.1	36.7	57.0	1.14	—	28.6	30.8
55	0.416	61.3	40.8	59.8	1.47	—	39.5	42.8
88	0.656	62.5	41.6	59.1	1.70	—	47.6	54.6
125	0.862	61.2	41.8	60.7	1.76	—	49.9	58.7

## SUMMARY

The oxidation of cotton cellulose by chromic acid (dichromate in the presence of sulphuric acid) has been studied over a range of oxygen consumption up to more than an atom per glucose unit

Examination of the properties of the chromic acid oxycelluloses has shown that the copper number, the fluidity in cuprammonium hydroxide, the loss of weight on treatment with cold or hot dilute sodium hydroxide solution or with hot water, the ash content, and the hygroscopicity all increase with increasing oxygen consumption until the latter has attained a certain value, and thereafter remain almost constant, the Methylene Blue absorption, on the other hand, increases continuously throughout the range of oxidative attack investigated. The tensile strength falls as oxidation proceeds, the cotton being reduced to powder by an oxygen consumption of about 0.4 atom per glucose unit. The considerable ash content of the oxycelluloses is due to retention of chromium.

The nitrogen content of nitrocelluloses derived from the oxycelluloses falls with increasing degree of oxidation until the oxygen consumption is about 0.5 atom per glucose unit and then becomes constant. The nitrogen content at this stage indicates that the hydroxyl content of the most highly oxidized products is some 90 per cent of that of unoxidized cellulose.

The oxidation of cellulose by chromic acid leads to a progressive loss of weight, due to the formation of carbon dioxide, formic acid and unidentified soluble products which are capable of being further oxidized.

The oxidation of cotton by chromic acid does not produce any considerable dimensional changes, and has no effect on the X-ray diagram.

The relations between the properties of oxycelluloses prepared from mercerized cotton and the oxygen consumption are qualitatively similar to those found with oxycelluloses from unmercerized cotton, but the consumption of a given proportion of oxygen leads to higher values of the properties with mercerized than with unmercerized cotton.

It has been found that there is a relatively rapid fall in the chromic acid concentration during the initial stages of the oxidation of cotton, and this is ascribed to adsorption of the oxidant by the cellulose.

The results obtained in the investigation suggest that the oxidation of cellulose by chromic acid is largely confined to the inter-crystalline regions in the cellulose.

Some of the experimental work was done by Miss E. H. Elding

## REFERENCES

- <sup>1</sup> Clibbens and Ridge *Shirley Inst Mem*, 1927, 6, 1, or *J. Text Inst*, 1927, 18, 1135.
- <sup>2</sup> Clibbens and Ridge *Shirley Inst Mem*, 1928, 7, 85, or *J. Text Inst*, 1928, 19, 1389.
- <sup>3</sup> Davidson *Shirley Inst Mem*, 1937-38, 16, 29, or *J. Text Inst*, 1938, 29, 1185.
- <sup>4</sup> Davidson *Shirley Inst Mem*, 1939-40, 17, 83, or *J. Text Inst*, 1940, 31, 181.
- <sup>5</sup> Davidson *Shirley Inst Mem*, 1941, 18, 69.
- <sup>6</sup> Hibbert and Parsons *J. Soc. Chem. Ind.*, 1925, 44, 473T.
- <sup>7</sup> Britton *Analyst*, 1924, 49, 130.
- <sup>8</sup> Birtwell, Clibbens and Ridge *Shirley Inst Mem*, 1924, 3, 321, or *J. Text Inst*, 1925, 16, 113.
- <sup>9</sup> Neale *Nature*, 1935, 135, 583.
- <sup>10</sup> Neale and Stringfellow *Trans. Faraday Soc.*, 1937, 33, 881.
- <sup>11</sup> Seck *Melland Textilber*, 1932, 13, 314.
- <sup>12</sup> Staudinger and Sohn *Naturwiss.*, 1939, 27, 548, *Ber. deut. chem. Ges.*, 1939, 72, 1709.

# THE JOURNAL OF THE TEXTILE INSTITUTE

## TRANSACTIONS

### 11—THE TRANSMISSION OF HEAT THROUGH TEXTILE FABRICS

By W HOWARD REES, M.Sc., A.Inst.P.

(British Cotton Industry Research Association)

*Copyright by the Textile Institute.*

#### (1) INTRODUCTION

Warmth may not be the only quality for which garments are worn, but it is certainly one of the most essential ; physical properties such as tensile strength and waterproofness will usually be of secondary importance to the ability of a garment to serve as a thermal insulator

The wearer of every garment has a fairly decided opinion on its "warmth", general experience or prejudice has been regarded as sufficient to decide the merits of the various types of fabric. Wool has always been regarded as "warm", cotton and linen as "cold", largely on account of the weight, thickness and structure of the fabrics commonly made from these fibres. Any fibre material conducts heat more readily than does still air, and any "warm" material will include a considerable amount of air in its structure. When we speak of the "thermal conductivity" of a textile fabric we really mean the thermal conductivity of a disperse system consisting of textile substance and air, and not that of a massive substance, say of cellulose. In considering the flow of heat through such a heterogeneous system, it must be realised that the term "thermal conductivity" does not have its usual precise physical meaning, for, in addition to pure conduction, we also have transfer of heat by convection and radiation through the spaces in the fabric. Further, since textile materials are hygroscopic, there will be transmission of heat due to evaporation and condensation of moisture, so that, altogether, the transfer of heat is a complicated process.

The purpose of the present work is to measure the thermal transmission of fabrics under conditions approaching as nearly as possible those encountered in actual use, while retaining strictly specified conditions and measuring a simply definable quantity. With this end in view, a search of the literature was made. A review of the various methods employed is given by Marsh<sup>1</sup> and by Black and Matthew<sup>2</sup>. After considering these methods, it was decided to employ the constant temperature method in which the power required to maintain a body at a known constant temperature above that of the surroundings is measured. This method has the advantage that measurements of heat are replaced by those of electrical energy, and can therefore be made more accurately. The apparatus designed for this work is described in the following section.

The simplest form of the physical measurement of thermal transmission is that of the conduction of heat between two plates, one hot and one cold, with the specimen placed between and in good thermal con-

tact with both plates. These are the usual conditions adopted in measuring the thermal conductivity of a material, and it is possible to make such measurements on the apparatus about to be described. Some previous studies on fabrics have been made under such conditions<sup>3</sup>, and one may find conditions of service that approximate to them, but these are not the conditions under which the thermal insulation is most important. The protective function of a garment or set of garments is called upon more frequently and more urgently when its surface is exposed, and particularly in cold draughts. In the present experiments, instead of the heat transmitted through the fabric being conducted away by a cold metal plate, a current of air is directed on to the outer surface, as in the recent work of Niven and Babbitt<sup>4</sup>, where, in a definite attempt to simulate room conditions, a current of air of various known velocities was directed on to the fabric under test. This is a more searching test of the ability of the fabric to immobilise the air in its interstices, on which its protective value mainly depends. An outer cold plate immobilises air that the fabric could not immobilise, e.g. a coarse open mesh would appear to have greater insulating value than it would have in service.

The effect of the evaporation of perspiration from the human skin upon the thermal insulation given to it by a fabric has been passed over by many workers owing to the difficulty of imitating this action in an experiment. The view has been advanced that this question need not be considered because the skin is usually dry in winter when warm clothing is most necessary. But this is an exaggeration and, for the full understanding of the "warmth" of a garment, it is certainly necessary to study the effect of a damp body. Tests carried out with both a temperature and a relative humidity gradient through the fabric would simulate practical conditions.

The present apparatus was designed to allow easy modification to a form in which this type of heat loss can be measured. Heat loss under conditions of uncontrolled complexity does not give a reliable index of practical insulating value. One may wrap a vessel, containing warm water, with the material and observe the rate of loss of temperature, e.g. in Kata-thermometer work<sup>2</sup>. This method has been used rather widely and, in general, the results run roughly parallel to those obtained on the present apparatus. It is simple mechanically, but not physically or thermally. The various types of heat loss combine to give the result observed, and combine in unknown degree varying with the size of the instrument and other details. Such tests may be made under conditions approaching those of service, but the meaning of the results will be limited to the particular apparatus.

With the present apparatus, the conditions can be controlled and measured so that the results have definite meaning not limited to the particular instrument, and the several kinds of heat loss can be separated or combined to reproduce the essential features of the conditions of service of a particular material.

## (II) THE APPARATUS

A circular horizontal plate, surrounded by a guard-ring, is heated to a temperature approximately equal to that of the human skin. The guard-ring is heated to identically the same temperature, so that all the heat is flowing normally to the plate. The rate of flow of heat through the plate is then measured by the rate of supply of electrical energy required to maintain the plate at this constant temperature.

The essential features of the apparatus are shown diagrammatically in Fig 1. An open brass cylindrical vessel (A) is contained in a larger coaxial vessel (B) also cylindrical, and separated from it by a narrow air-gap. A circular copper plate (C) is fixed to the rim of the vessel A, and an annular copper plate (D) to the rims of vessel B. When in position, the circular and annular plates are in the same plane. The vessel A is the calorimeter, and the copper plate fixed to its rim is the hot plate of the apparatus; the annular plate fixed to the rims of the outer vessel B acts as a guard-ring. Both vessels are filled with water (previously boiled to make it air-free) which may be heated electrically.

The temperature of the hot plate is measured by means of a fine wire thermocouple (E) fixed to its outer surface. Differential thermocouples fixed to the plate and the guard-ring indicate any difference of temperature between them. One of these (F) is shown in the figure.

The fabric under test (H) is clamped between two similar brass frames (I) mounted on three vertical threaded rods, so that the fabric may be supported at any desired distance from the hot plates, or in contact with them. The arrangement takes a flat sample 7" square, the actual measurement being made on a circular portion 2" in diameter in the middle of the sample.

The calorimeter and the outer vessel carry heating elements consisting of Nichrome wire wound on glass frames (see Fig 2). The resistance of the calorimeter coil is about 3 ohms, and that of the outer coil about 17 ohms. The leads to these coils are heavy insulated copper wires.

The method adopted for stirring the water inside the instrument is to keep glass spheres immersed in the water in motion. The arrangement is shown in Fig 3 and Fig 2C and 2D. The instrument is fixed to a base plate mounted on spiral springs. To this base plate is fixed a vertical arm which fits into a slot in a crank rotating in a horizontal plane. The instrument is thus given a rolling motion about a vertical axis which keeps the glass spheres rolling continuously inside the vessels. Ten revolutions per minute with the plates inclined at 5° to the horizontal produces efficient stirring.

#### **The Hot Plates**

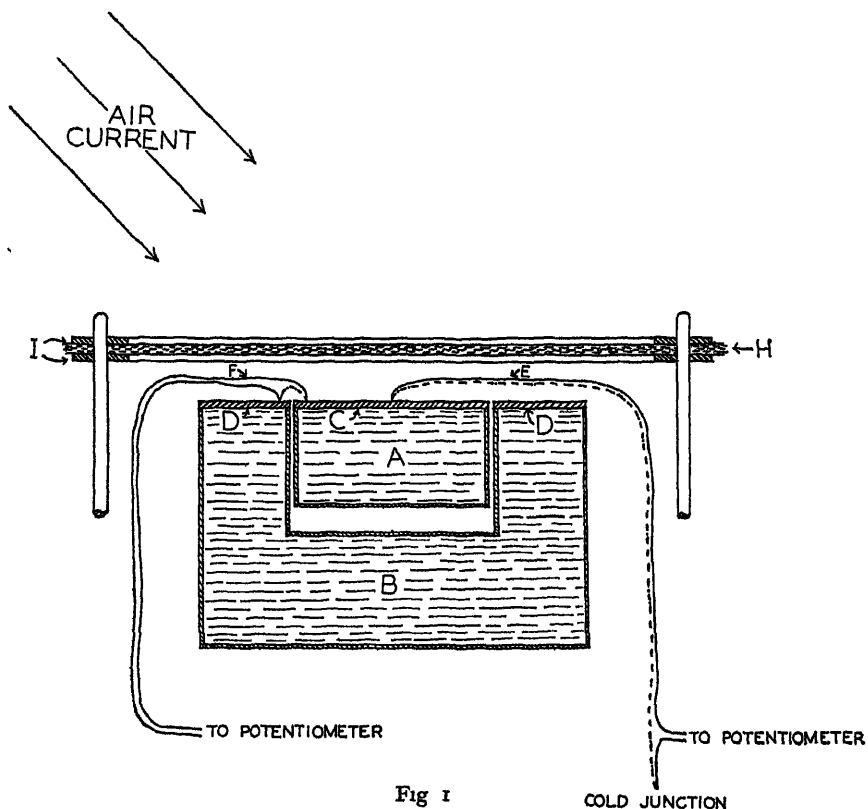
The instrument was devised for two distinct investigations, using methods (1) in which a temperature gradient exists through the fabric, and (2) in which both a temperature and a moisture gradient exist through the fabric. The results given in the present publication apply to method (1) only, a later publication will deal with the results of method (2).

Method (1) may be called the "dry plate" method, and for this purpose the hot surfaces consist of copper plates which are fixed to the rims of the calorimeter and guard-ring cylinders with Necol cellulose cement. The calorimeter and guard-ring plates are each fitted with a valve which allows the escape of air while the instrument is being filled with water from an external reservoir. When filled, the valves are closed flush with the surface of the plates. The copper-Constantan thermo-junctions are soldered to the surface of the plates, and the insulated leads are cemented in narrow grooves cut in the plates so that they do not interfere materially with their flat assembly.

Method (2) is the "wet plate" method. The copper plates are replaced by porous plates of the same dimensions, which are cemented to the rims



of the vessels. A suitable arrangement keeps the calorimeter and guarding cylinder filled with water, and the porous plates form an "unspillable" water surface. The rate of evaporation may be determined by measuring the rate at which water is supplied to the instrument. By using a porous plate, the moisture permeability of a fabric may be determined, and as this plate may also be made a "hot plate" by heating the water as before, the rate of transmission of heat through the fabric may be measured under



conditions which provide a moisture gradient through the fabric. The amount of water which has evaporated being known, the amount of heat lost in evaporating it may be found and allowed for. The surface of the fabric remote from the plate is exposed to air under certain conditions of temperature, relative humidity and velocity, which may be varied.

#### Control of Environment

In order to ensure constant and reproducible conditions, the instrument is enclosed in a large air-tight box. The air temperature inside the box is maintained at a constant value (25° C.) by means of a mercury-toluene thermostat. Inside the box, an electric fan blows a stream of air over a saturated solution of a salt, and by this means the humidity of the air is kept constant. It is possible to carry out heat-loss tests in still air by screening the plates from the moving air. Such conditions, however, are difficult to maintain, and tests are usually carried out with a current of air, moving at known speed and impinging on the sample at an angle of 45°

with its surface. For this purpose, a variable speed fan is mounted inside the box, and the speed of the air current measured by a vane anemometer

#### Energy Control

The current for both the calorimeter and guard-ring heaters is obtained from the A C. mains supply, two transformers providing the desired potential drop across the coils. Ordinary rheostats are used to regulate the currents, and either circuit can be controlled independently of the other. The resistance of the calorimeter coil was accurately measured and checked at frequent intervals. The electrical circuit is shown in Fig. 4.

#### Temperature Measurement

Copper-Constantan thermocouples are employed in the measurement of temperature, a vacuum flask filled with ice being used as the cold junction

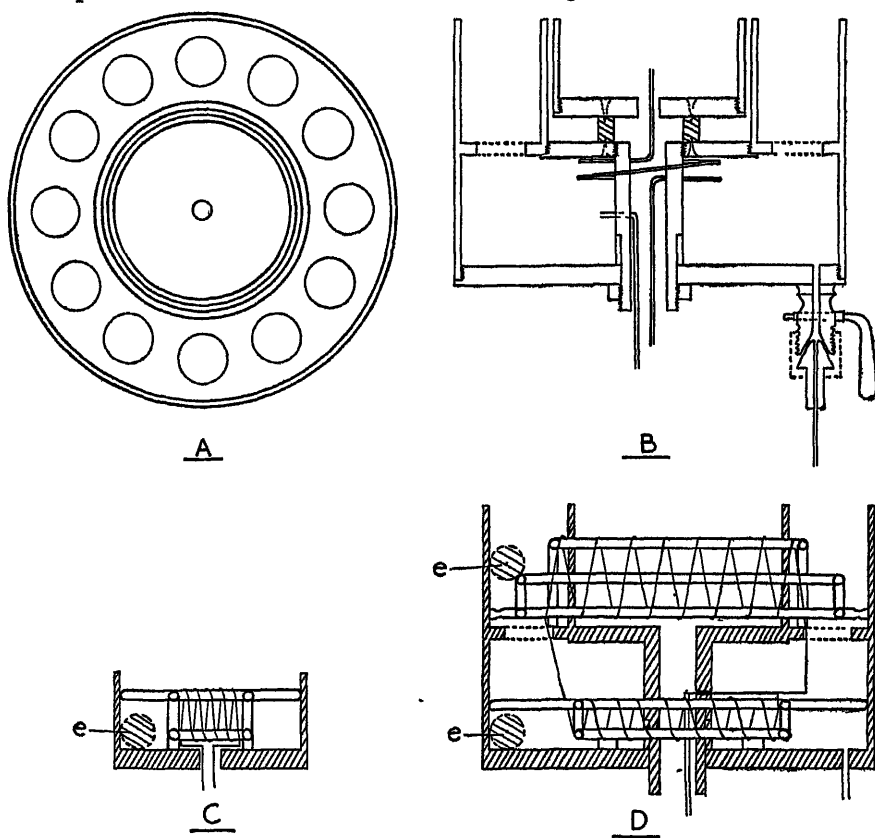


Fig. 2

Diagrams of the Calorimeter and Guard Rings, showing Heating Coils.

- A Plan
- B Section showing water supply pipes (ebonite supports shaded)
- C Section of calorimeter showing heating coil wound on glass frame
- D Section of guard ring showing upper and lower heaters wound on glass frames.
- e Glass spheres for circulating water.

The potentiometer method is employed. As mentioned, differential thermocouples are used to detect any difference of temperature between the hot-plate and the guard-ring. The thermocouple circuit is shown in Fig. 5.

### The Preheater

When tests were made with thick fabrics, it was found that they took a very long time to attain equilibrium on the apparatus, probably due to the gradual drying out of the fabric. It was also found that warming the sample previous to testing reduced the time of equilibration, and accordingly, a

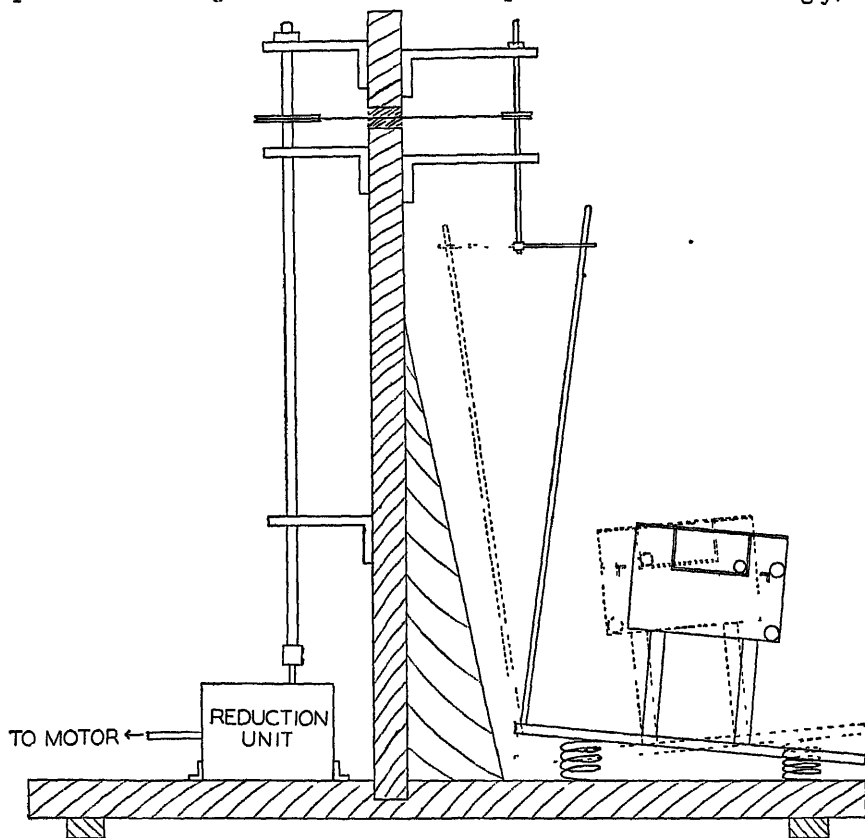


Fig 3 Diagram of Stirring Arrangement One-fifth full size

$T_1$  Transformer (230-24 volts)  $R_1$  380 ohms (max)  
 $T_2$  Bell transformer (230-6 volts)  $R_2$  50 ohms (max)  
 A, Ammeter.

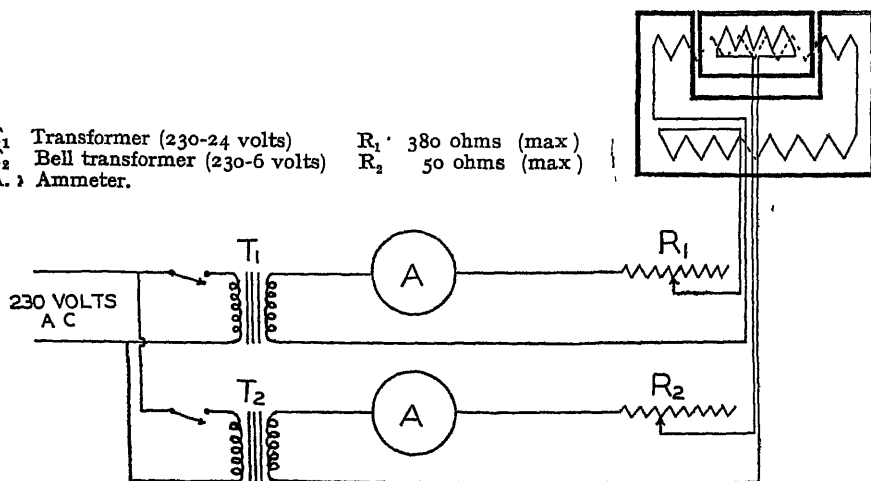


Fig 4

preheater was constructed for pre-conditioning the sample under the conditions of testing. A rectangular brass vessel is filled with water which is heated electrically to a temperature controlled by a thermostat. This temperature is so adjusted that the flat surface on which the sample is laid is at the same temperature as the hot plate of the testing apparatus. The other surface of the sample is exposed to moving air of the same humidity as that used in the tests, and it is allowed to condition for several hours before testing.

#### **The Two-plate Method of Testing**

As already mentioned, tests are usually carried out with the surface of the sample remote from the hot plate exposed to air moving at known speed in a fixed direction, the rate of loss of heat through the fabric under these conditions being measured. The apparatus can readily be modified to a form in which measurements of thermal conductivity are made by bringing a cold plate into contact with the previously exposed surface of the fabric and measuring the temperature gradient across the fabric by means of a thermocouple attached to the cold plate. This plate, shown in Fig 5 (D) consists of a circular copper plate surrounded by a guard-ring, the narrow gap between them being filled with an annular ring of bakelite. The dimensions of the components are the same as those of the hot plates of the instrument, and a copper-Constantan thermojunction is soldered to the centre of the plate as with the hot plate.

#### **Method of Experiment**

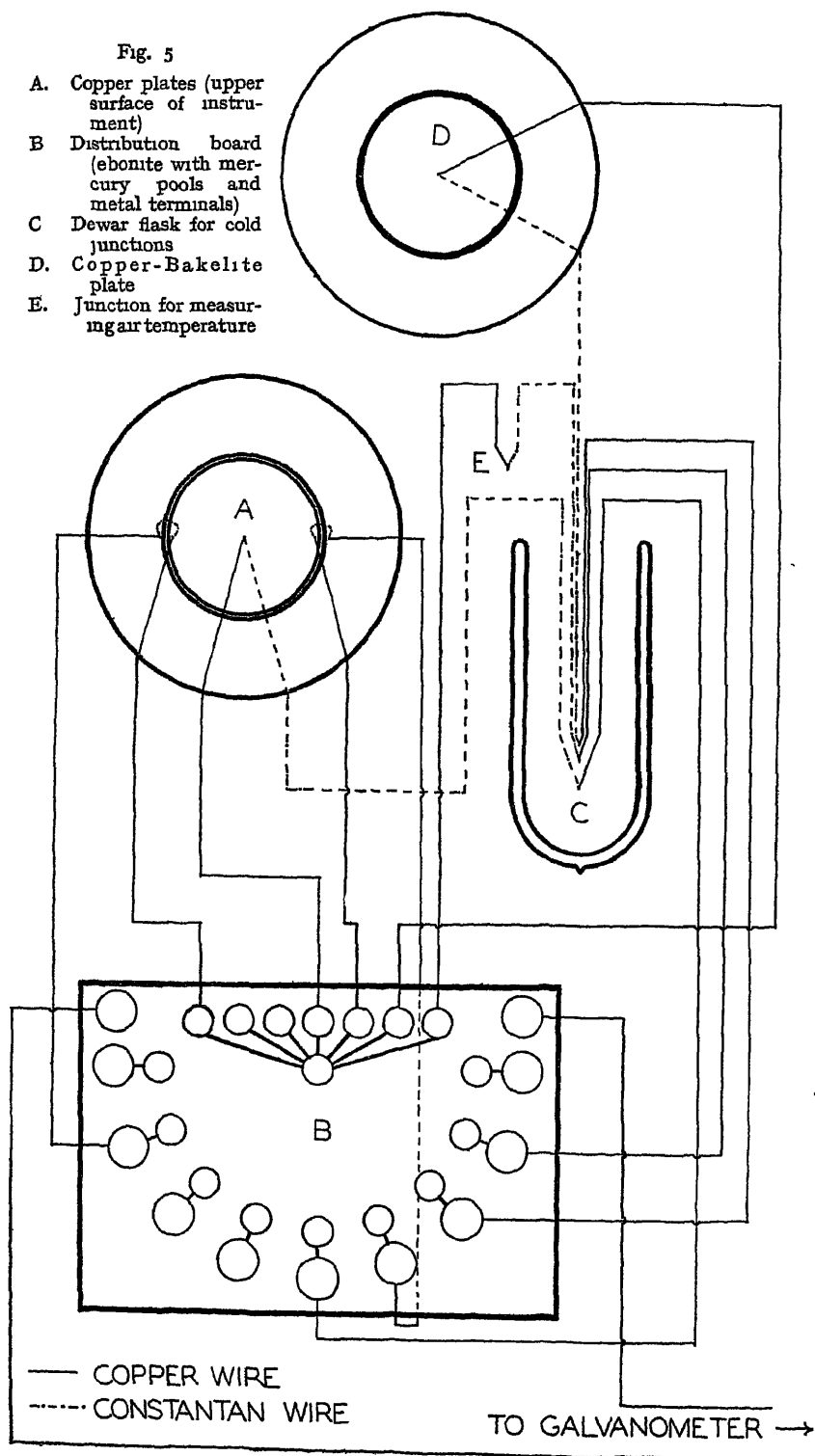
The conditions of air temperature, humidity and velocity having been fixed, the apparatus is heated to the desired temperature, and the sample then quickly transferred from the preheater to the apparatus where it is clamped in position, either in contact with the plates, or at some distance from them. The heating currents are carefully adjusted until the central plate and guard-ring reach a constant temperature very near to body temperature as indicated by the thermocouple on the outer face of the central plate and by zero indications on the differential couples. When a steady state is attained, readings of the heating current, hot plate temperature and air temperature are taken and, if the cold plate is being used, the temperature attained by its face in contact with the fabric.

### **(III) RESULTS OF WORK WITH THE DRY PLATES**

It was considered advisable to check the value of heat flow from the apparatus as measured by the instruments employed, and for this purpose the two-plate method mentioned above was used to measure the absolute thermal conductivity of a reproducible solid material. Tests were made on ebonite and on plate glass, the latter being the actual sample whose thermal conductivity had been measured at the National Physical Laboratory. With ebonite, three circular discs of thicknesses  $\frac{1}{8}$ ",  $\frac{1}{4}$ " and  $\frac{3}{8}$ " were used, and with the plate glass, six discs of thickness about  $\frac{1}{8}$ ". In each case, a film of glycerin was used to ensure good thermal contact between the sample and the hot and cold plates. The thickness of the glycerin film was measured by means of a travelling microscope and found to be approximately 0.05 mm, and a correction for the temperature drop across the film was made in each case. The mean values obtained were 0.000389 and 0.00207 cal/cm<sup>2</sup> sec<sup>-1</sup>. °C<sup>-1</sup> for ebonite and for plate glass, respectively. The

Fig. 5

- A. Copper plates (upper surface of instrument)
- B. Distribution board (ebonite with mercury pools and metal terminals)
- C. Dewar flask for cold junctions
- D. Copper-Bakelite plate
- E. Junction for measuring air temperature



value given by the National Physical Laboratory for the same glass was  $0.0021 \text{ calorie cm}^{-1} \cdot \text{sec}^{-1} \cdot ^\circ\text{C}^{-1}$ . These results confirm the validity of the thermal measurements made on this apparatus.

Under the conditions of testing adopted (one side of the fabric exposed to moving air), the rate of passage of heat through the central portion of the fabric from the metal plate to the air is measured. Preliminary experiments showed that this is accurately proportional to the difference in temperature between the plate and the air, and accordingly the results are expressed as the rate of passage of heat in calories per second per square metre per degree (Centigrade) difference in temperature between the plate and the air. The lower this figure, the better is the insulation afforded by the fabric.

If the rate of heat loss from the uncovered heater is also measured under the same conditions as when covered, the insulation afforded by the fabric may be defined by a quantity called the thermal insulating value, given by the expression

$$\left\{ 1 - \frac{\text{Heat lost by covered heater}}{\text{Heat lost by uncovered heater}} \right\} \times 100\%$$

that is, the percentage reduction in heat loss brought about by covering the heater with the fabric.

#### Effect of Closeness of Fit

It has often been shown that the degree of closeness of fit of a fabric on a warm body is an important factor in determining the thermal insulation given to the body. This was the first point to be investigated. The lower supporting frame was arranged to be dead level with the hot plates, and a cotton blanket was placed on the instrument smoothly but under no appreciable tension and clamped in position. The thermal insulating value (T.I.V.) of the blanket under the conditions of wind-speed, humidity and temperature adopted was 62.7 per cent. The frame was now lowered slightly below the level of the plates, so that the fabric was under slight tension; the T.I.V. was now 61.1 per cent. The frame was lowered slightly more, and the T.I.V. fell to 60.0 per cent., so that increasing the tension lowered the insulating value of the blanket. The frame was now raised to a distance 0.05 inch above the plates, an impervious screen being fitted to the guard-ring cylinder to ensure that no draught penetrated the space between the hot plate and the fabric, and the T.I.V. was found to have risen to 67.1 per cent. The gap between the fabric and the hot plate was increased in steps, and the insulation value was determined at each stage. The T.I.V. was found to increase steadily to a maximum, and then to decrease, owing to convection. The results obtained with a cotton and with a rayon and cotton mixture blanket are given in Table I.

Table I

Air space, inch	0	0.05	0.15	0.20	0.25	0.30	0.35	0.40
T.I.V. { Cotton blanket	62.7	67.1	73.1	75.7	77.1	78.2	78.7	77.4
% { Rayon blanket	62.4	65.9	71.8	74.0	75.8	77.4	77.9	76.6

Great care has thus to be taken, in making tests at close fit, that the supporting frame is strictly level with the hot plate.

#### Effect of Wind Speed upon Heat Transmission

The heat loss through an ebonite sheet and through a number of different fabrics in still air and in air moving at various known speeds was measured,

and the results are shown graphically in Fig 6. The wind speeds given are those at a point (12 cms,  $45^\circ$ ) from the centre of the sample. The graphs for the ebonite sheet and for the bare plate appear to be straight lines. Curve 1 is for a thin cotton netting of very open structure, and above a wind-speed of 1 ft/sec, this also appears to be linear. This fabric was very open and afforded little resistance to the passage of air through its

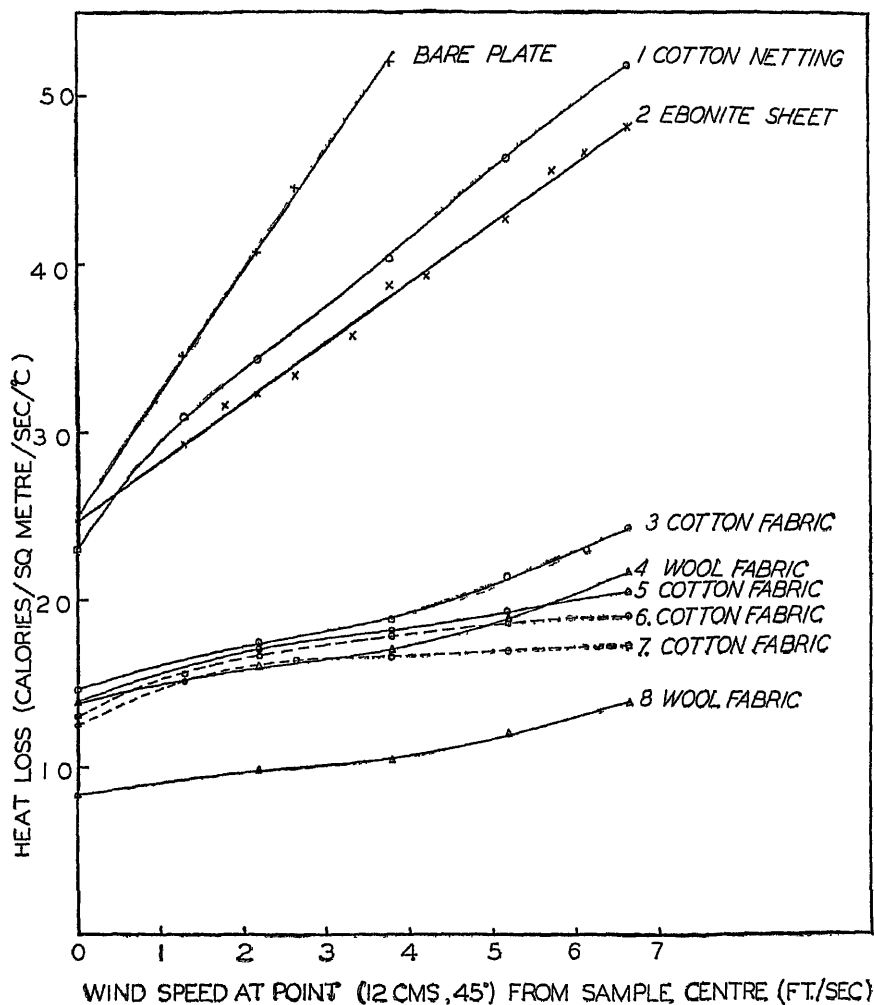


Fig 6  
Variation of Heat Loss with Wind Speed

structure. Curves 3, 4 and 8 show a rapid increase of heat loss at the higher wind speeds which is not apparent in curves 5, 6 and 7. The fabrics of curves 5, 6 and 7 are closely woven, whilst those of curves 3, 4 and 8 have a much more open structure, and at the higher wind speeds the air will be circulated in the interstices of the loosely woven fabrics, resulting in greater heat loss.

**Effect of Relative Humidity upon Heat Transmission**

By using saturated solutions of various salts, the relative humidity of the atmosphere in which the tests are made can be varied within certain limits. Tests were made with a wool, a cotton and a rayon blanket, and a bleached cotton cloth in atmospheres of 33, 53, 65, 75 and 88 per cent R.H., and the results are plotted in Fig 7. An increase of 55 per cent. R.H. increased the heat loss of the wool blanket by about 10 per cent and of the

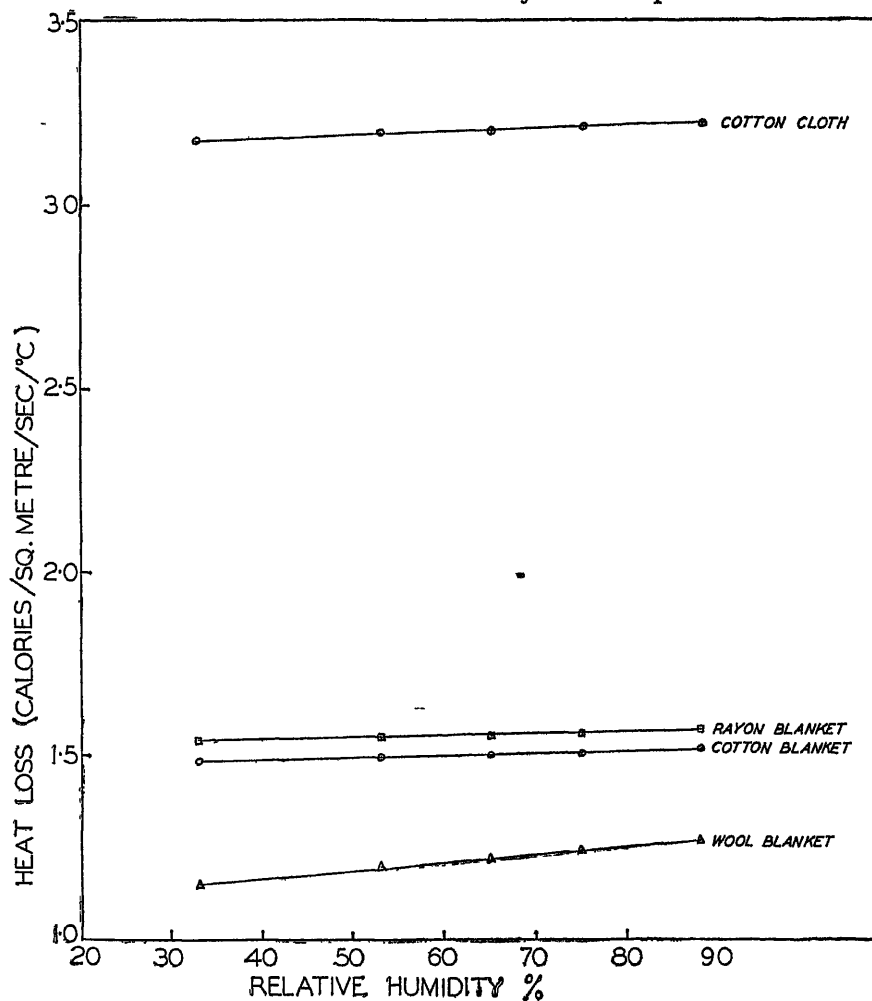


Fig 7

Variation of Heat Loss with Humidity

[Wind speed 2.2 ft/sec at a point (12 cms., 45°) from the centre of the sample]

cotton blanket by about 3 per cent. The conclusion is that while increasing the humidity increases the heat loss, the effect of such changes of humidity as are likely to be met with in service upon the thermal insulation of a fabric is small, provided that there is no evaporation from the insulated body.

**Comparison of Fabrics**

From the results of the experiments already described, the conditions for the comparison of different fabrics were chosen. It was decided to make



the tests with the fabrics at zero tension and at close fit on the hot plate, the pressure being virtually that due to the weight of the sample itself resting on a horizontal surface. All tests are made in an atmosphere of 65 per cent R.H. and  $25^{\circ}\text{C}$ , with a current of air impinging on the sample in a direction at  $45^{\circ}$  to its surface and having a speed of 2.2 ft/sec. at a point (12 cms.,  $45^{\circ}$ ) from the sample centre

The heat loss values were plotted against thickness and weight per unit area (Figs. 8 and 9, respectively). The thicknesses used are those under a pressure of 0.001 lb./sq. inch. Measurements of thickness were made under pressures of 0.5 and 10 lb./sq. inch and plotted against the heat loss values but gave more scattered points. This would indicate that the actual thick-

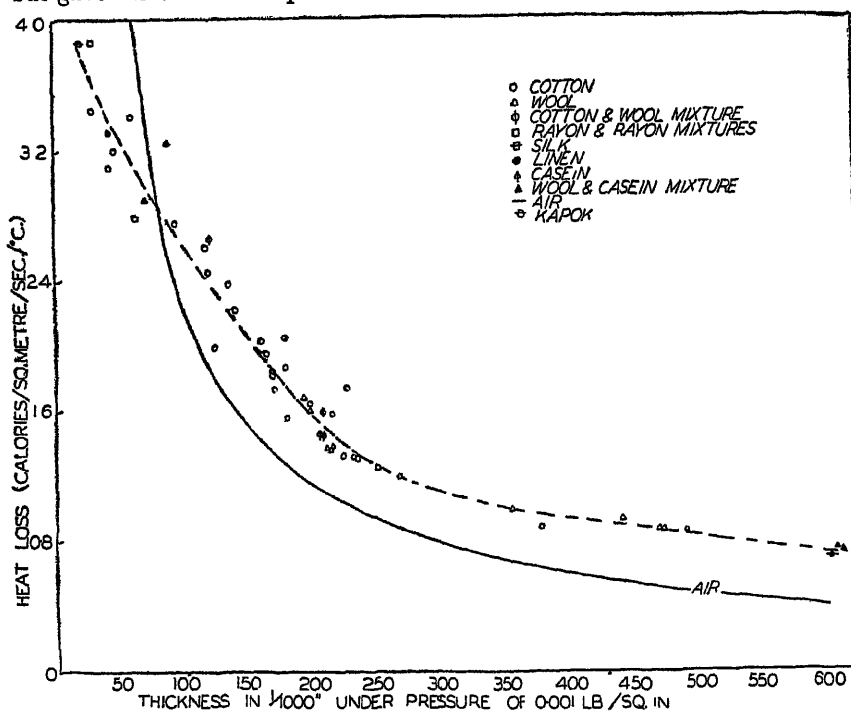


Fig. 8

#### Variation of Heat Loss with Thickness of Material

[Sample at close fit Wind speed 2.2 ft/sec at a point (12.5 cms.,  $45^{\circ}$ ) from the centre of the sample Air at  $25^{\circ}\text{C}$  and 65 per cent R.H.]

(The broken line is a freehand curve drawn to indicate the normal empirical relation between heat loss and thickness of a fabric, to facilitate an estimate of its probable performance from a measurement of thickness alone. The full line is the theoretical curve for air, see text.)

ness of a fabric under the conditions of test is important in determining its thermal insulation. The dependence of the thermal insulation of a fabric upon its thickness, irrespective of the type of fibre used in its make-up, is made apparent by Fig. 8. Thickness may not be the only factor which determines the thermal insulation of a fabric, but it is certainly one of the most important. The heat loss through a fabric is greater than through an equal thickness of air, conduction through the actual fibres being a contributing factor. The curve marked "Air" in Fig. 8 relates the heat loss by conduction across a layer of air with the thickness of the layer when a

temperature difference of  $1^{\circ}\text{C}$ . exists between the boundaries of the layer. This is calculated from the usual expression for thermal conductivity, assuming  $K_{\text{air}} = 0.00006$  c g s. units. The equivalent air thicknesses of the samples were estimated and compared with the fabric thickness. For fabrics of thickness greater than about 100 mils, the equivalent air thickness is less than the fabric thickness by about 20 per cent at 100 mils fabric thickness, and about 40 per cent. at 400 mils fabric thickness.

With very thin fabrics the points are rather more widely scattered, and the heat loss values appear to be lower than would be expected from the

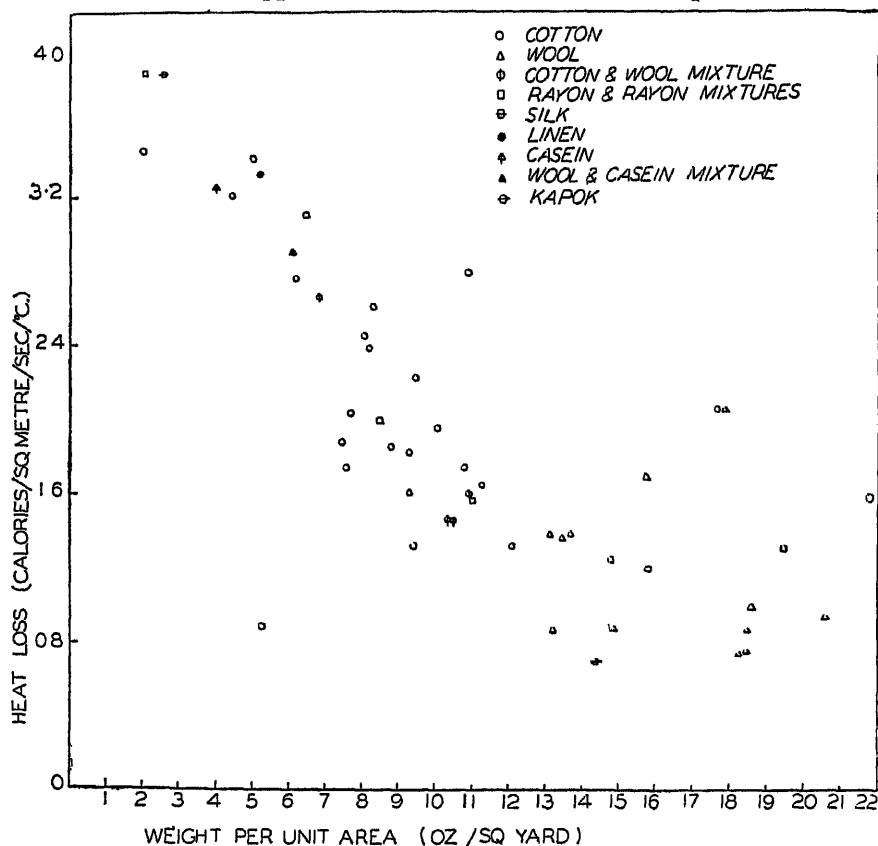


Fig. 9

Plot of Heat Loss against Weight per Unit Area of Material.

Samples at close fit Wind speed 2.2 ft/sec at a point (12.5 cms,  $45^{\circ}$ ) from the centre of the sample Air at  $25^{\circ}\text{C}$ . and 65 per cent R.H.]

shape of a mean curve through the points of higher thickness. These fabrics are so light that in all probability a layer of air is trapped between them and the hot plate, which would account for their seemingly high thermal insulation.

In considering deviations from a mean curve through the points, it was found that, in general, fabrics of low density had a smaller heat loss, and fabrics of high density a greater heat loss than the average. With the dense fabrics, the heat loss by conduction through the fibres will make a greater contribution to the total heat loss.

In Fig. 9, heat loss values are plotted against weight per unit area. The points are considerably more scattered than when heat loss values are plotted against fabric thickness, though, as one would expect, the heavier samples are generally the warmer as such samples are usually also thicker.

These results suggest that a fabric of given insulating value could be constructed from any of the textile fibres by making it sufficiently thick. In service, wool appears to be the material mostly used for making thick fabrics, and has thus earned the reputation for being warmer than other textile materials. It is, of course, a "lofty" fibre (with considerable elastic resistance to flexure) and lends itself easily to the construction of thick fabrics of low density.

The experiments of Speakman and Chamberlain<sup>1</sup> and of the staff of the Scientific Laboratory of the Rayon Factory of the I. G. Farbenindustrie A-G, Wolfen<sup>5</sup>, on the thermal conductivity of textile fibres show that the various textile materials do differ in respect of the thermal conductivities of their fibres. However, with a loose structure such as a textile fabric, such differences may be masked by the effect of the air contained in the structure.

#### Thermal Conductivity of Fabrics

As already mentioned, the conductivity of a fabric may be measured on the present apparatus by placing the fabric between two metal plates, one hot and one cold, and measuring the difference of temperature between their inner surfaces when equilibrium is established. Though the conductivity of a fabric so measured may not be directly applicable to the insulating value of the fabric under the more important conditions of service such measurements are of interest in the interpretation of the heat loss value under the standard conditions of testing. Some results are given in Table II. The tests were made with the samples under a pressure of 0.08 lb per square inch.  $H_1$  is the heat loss through a sample in calories per square metre per second per degree Centigrade difference of temperature between

Table II

Sample	Thickness under 0.001 lb/sq. in., mils	Density (gm/cc)	$H_1$	$H_2$	$K$	TIV %
Wool fabric	199	0.05	2.07	1.61	0.000095	62.4
Wool fabric	216	0.10	1.71	1.38	0.000120	67.7
Wool and rayon fabric*	252	0.12	1.39	1.24	0.000095	70.9
Wool and rayon fabric†	64	0.26	3.12	2.79	0.000147	34.7
Rayon and cotton fabric‡	182	0.08	1.90	1.56	0.000140	63.5
Rayon and silk fabric§	31	0.10	3.39	3.87	0.000210	9.5
Silk fabric	22	0.18	3.47	3.86	0.000170	9.7
Linen fabric	45	0.17	3.43	3.32	0.000220	22.4
Cotton fabric	170	0.08	2.25	1.82	0.000180	57.4
Cotton fabric	31	0.09	3.08	3.44	0.000180	19.5
Multiple cotton fabric	214	0.33	—	—	0.000245	—
Multiple cotton fabric	156	0.45	—	—	0.000276	—
Multiple cotton fabric	163	0.45	—	—	0.000283	—
Multiple cotton fabric	301	0.33	—	—	0.000269	—
Multiple cotton fabric	184	0.53	—	—	0.000316	—

\* Acetate staple fibre (40%), acetate rayon (35%) and wool (25%).

† Acetate rayon (50%) and wool (50%).

‡ Viscose staple fibre weft, cotton warp.

§ Acetate rayon warp, crepe silk weft.

the hot plate and the air under the two-plate method of testing.  $H_1$  is the corresponding heat loss without the top plate, one face of the fabric being exposed to wind of speed 22 ft/sec at (12 cms,  $45^\circ$ ) from its centre. The thermal insulating values given in column 7 were measured without the top plate. The thermal conductivity ( $K$ ) is given as the rate of passage of heat through unit area of the sample per unit temperature gradient across it, this gradient being the difference of temperature between the surfaces of the hot and cold plates in contact with the sample divided by the distance between these surfaces.  $K$  is given in calories  $\text{cm}^{-1} \text{sec}^{-1} ^\circ\text{C}^{-1}$ .

It will be seen that with fabrics having the same constituent, the less dense fabrics have the lower conductivity. It is also seen from columns 4 and 5 that, in some cases, the heat loss through a fabric under the standard conditions of testing ( $H_2$ ), i.e. with one surface exposed to wind, is greater than the heat loss measured by the two-plate method ( $H_1$ ) with the same external conditions. The upper plate immobilises air that the fabric itself could not immobilise, so that, in the second case, the fabric appears to have a higher insulating value than it would have when exposed to wind.

In most cases,  $H_1$  is greater than  $H_2$ . This may be explained by the fact that in the two-plate method of testing the fabric is under pressure, so that its thickness is considerably lower than its value under the standard conditions of testing.

#### Multiple Layers of Fabrics

The addition of successive layers of the same material will naturally increase the thermal insulation given to the hot body. Some of the results obtained are given in Table III. The fabrics were chosen merely in order to illustrate the effect of adding successive layers, the values for the cotton fabric are lower because the fabric itself was thinner.

Table III

No. of layers	T I V, per cent.			
	1	2	3	4
Wool fabric	68.1	83.8	89.2	92.0
Cotton fabric	35.2	65.7	76.6	—
Viscose staple fibre weft, cotton warp fabric	63.5	79.1	85.7	—

The thermal insulating value of a typical closely woven wool blanket (thickness 216 mils, density 0.10 gm/cc) was measured in a wind of speed 4 ft/sec at a point (12 cms,  $45^\circ$ ) from the sample centre. A thin linen cloth (thickness 45 mils, density 0.17 gm/cc) of close structure was then placed over the blanket, and the thermal insulating value of the combination measured. The tests were then repeated with an open-weave cellular wool blanket (thickness 199 mils, density 0.05 gm/cc) in place of the closely woven wool one, the same linen cloth being used. The results are shown in Table IV.

Table IV

Sample	T I V.
	per cent
Typical wool blanket	73.3
Typical wool blanket and linen cloth	76.0
Cellular wool blanket	64.8
Cellular wool blanket and linen cloth	74.0

It is seen that the addition of the linen cloth produced a greater increase in thermal protection in the second case. With the single blankets, the cellular sample has a relatively poor insulation owing to the air being circulated in its open structure. When covered, however, the air is immobilised within the fabric, which accounts for the relatively large increase in thermal insulating value. An open fabric, therefore, though it may afford poor insulation in a wind, may become an efficient insulator when covered with a closely woven fabric.

#### The "Cold Feel" of Fabrics

It was frequently observed during tests on the heat loss through fabrics that the temperature of the hot plate dropped slightly when the fabric was first brought into contact with it. This is due to the "coldness" of the sample and is, of course, greater the lower the initial temperature. To study the effect, all samples were pre-conditioned at 25°C. and 65 per cent. R.H.

This effect varies markedly in different fabrics, and may be an important feature as regards comfort of putting clothing on next to the skin. A record of the initial change of temperature of the hot plate when the specimen is first applied gives a measure of this cold feel or chilling effect of the material. The results obtained are shown in Fig. 10. Wool and cotton blankets showed no chill effect and a wool blanket warmed up most quickly. The chill effect was quite marked with a smooth bleached cotton cloth; a similar linen cloth showed less chilling, a silk one about the same, and a cloth consisting of acetate rayon and silk much more.

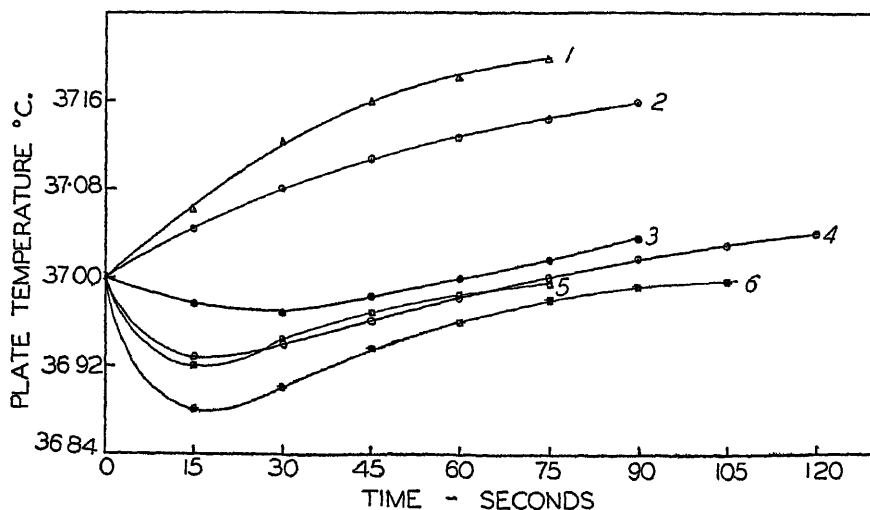


Fig. 10

"Cold Feel" of Fabrics Samples conditioned at 25°C. and 65 per cent. R.H.]

(1) Wool blanket (thickness 180 mils), (2) Cotton blanket (121 mils), (3) Linen cloth (45 mils), (4) Bleached cotton cloth (48 mils), (5) Silk cloth (22 mils), (6) Rayon and silk cloth (31 mils).

N.B.—Particulars of most of the fabrics mentioned in Tables II and III and in Fig. 10 are given in the Appendix and can be identified from values of thickness or T.I.V.

## SUMMARY

An apparatus is described for the measurement of thermal transmission through textile fabrics under conditions which simulate those of service. The apparatus may be modified to a form in which measurements may be made with both a temperature and a moisture gradient through the fabric. Results are given of tests with a thermal gradient only.

A further modification of the apparatus enables the absolute thermal conductivity of materials to be measured, and this has been done for the purpose of checking the apparatus. Measurements of the conductivity of various fabrics have also been made.

The rate of transmission of heat through a number of fabrics of different materials has been measured, and also the effect of ventilation and humidity upon this rate.

Measurements have been made of the increased insulation afforded by successive layers of a material, and of the "cold feel" or "chilling effect" of fabrics when first brought in contact with a warm body.

## REFERENCES

- <sup>1</sup> Marsh, M. C. *Journal Textile Institute*, 1931, **22**, r245-273.
- <sup>2</sup> Black, C. P., and Matthew, J. A. *Journal Textile Institute*, 1934, **25**, r197-224.
- <sup>3</sup> Speakman, J. B., and Chamberlain, N. H. *Journal Textile Institute*, 1930, **21**, r29-56.
- <sup>4</sup> Niven, C. D., and Babbitt, J. D. *Journal Textile Institute*, 1938, **29**, r161-172.
- <sup>5</sup> Staff of the Scientific Laboratory of the Rayon Factory of the I. G. Farbenindustrie A.-G., Wolfen. *Textilberichte, English Edition*, 1938, **19**, 161-164.

Received 10/7/41

## APPENDIX

Particulars of some of the fabrics used in this work are given in the following table

Description	Weight per sq yd (ozs)	Thickness under pressure of 0.001 lb/sq in (1/1000")	Ends	Picks	T I V (%)
*2/2 Twill, raised both sides, all wool, untreated	13.5	215	27	26	68.1
*2/2 Twill, raised both sides, all wool, untreated	13.2	216	26	30	67.7
*2/2 Twill, raised both sides, all wool, untreated	13.7	212	24	29	67.9
*2/2 Twill, raised both sides, all wool, dyed	17.9	180	26	24	52.0
*Leno, all wool, untreated	9.3	199	51	13	62.4
*2/2 Twill, raised both sides, all wool, dyed	15.8	195	20	23	60.5
Warp pile fabric, wool pile, cotton ground, warp and weft, dyed	14.9	470	43	56	79.5
Warp pile fabric, wool pile, cotton ground, warp and weft, dyed	13.2	473	28	62	79.5
2/2 Broken twill, wool-Lanital mixture, dyed	6.2	73	50	46	32.0
*Double cloth, raised both sides, cotton warp, grey, wool-cotton mixture weft	10.5	208	56	70	66.2
3/1 Twill, raised one side, cotton warp, wool weft, dyed	10.9	209	35	33	62.6
*Plain weave, raised both sides, cotton warp, grey, wool-cotton mixture weft	6.9	123	46	42	37.7
*2/2 Matt, raised both sides, all cotton, grey	8.1	121	43	56	42.6
*Plain weave, raised both sides, all cotton, grey	6.2	95	51	45	35.2
*2/2 Twill, raised both sides, all cotton, grey	8.3	119	46	56	38.8
*2/2 Twill, raised both sides, all cotton, grey	7.7	162	43	56	52.5
*2/2 Twill, raised both sides, all cotton, grey	8.2	136	24	47	44.2
*Plain weave, raised both sides, all cotton, grey	9.3	170	24	14	57.4
*Double cloth, raised both sides, all cotton, grey	8.8	170	42	54	56.8
*Double cloth, raised both sides, all cotton, grey	7.6	172	45	45	59.3
*Double cloth, raised both sides, all cotton, grey	21.8	217	40	44	62.8
*Plain weave, raised both sides, all cotton, grey	12.1	234	21	15	69.4
*Plain weave, raised both sides, all cotton, grey	9.4	226	23	18	69.2
Singles poplin, all cotton, bleached	4.5	48	56	66	25.0
3-pick Terry, yarns—dyed and bleached 2-fold ground warp, dyed and bleached singles terry warp, dyed singles weft—all cotton	7.5	181	46	50	56.2
3-pick Terry, yarns—2-fold terry and ground warp, singles weft, terry and weft dyed, ground bleached—all cotton	10.8	228	59	44	59.2
*Plain weave, raised both sides, all cotton, grey	17.7	180	25	20	52.0
Leno, all cotton, dyed	2.1	31	65	63	19.5
Warp pile fabric, all cotton, dyed	11.3	198	43	56	61.5
Warp pile fabric, all cotton, dyed	10.0	165	43	56	54.3
Warp pile fabric, all cotton, dyed	9.5	140	44	55	48.0
Warp pile fabric, all cotton, dyed	15.8	269	46	32	72.2
Knitted fabric 100% Casein	4.0	90	—	—	24.0
Poplin, all silk, dyed	2.6	22	121	79	9.7
Plain weave, flat acetate rayon warp, crepe silk weft	2.1	31	90	150	9.5
*Plain cloth, raised both sides, viscose staple fibre weft, cotton warp, grey	11.0	182	26	21	63.5
Plain weave, all linen, printed	5.2	45	37	35	22.4

Samples marked thus \* are suitable for blankets.

T I V values were measured under the standard conditions of testing, i.e., with the fabric at zero tension and at close fit on the hot plate, the other surface of the fabric exposed to an air current at 45° to its surface, and having a speed of 2.2 ft/sec at a point (12 cms, 45°) from the sample centre. Atmosphere, 65% R.H., 25°C.

# THE JOURNAL OF THE TEXTILE INSTITUTE

## TRANSACTIONS

### 12—THE BREAKING STRENGTH OF FABRICS

By P LAROSE

*Copyright by the Textile Institute*

**The "Half-Grab" Test and the relation between the results obtained in the "Grab," the "Half-Grab" and the "Strip" Test.**

The determination of the breaking strength is a regular routine test in the examination of most fabrics, and it is used regularly as an indication of quality or serviceability. For this reason, specifications for cloth generally contain a clause covering breaking strength requirements.

Two types of tests are widely used for determining the breaking strength of fabrics, the "strip" test and the "grab" test. In the strip method, a piece of the fabric is ravelled down to a pre-determined width, generally one or two inches, sometimes wider, and this ravelled strip is broken after being clamped in jaws wider than the strip. In the grab test the strip of cloth used is wider than the jaws in which it is clamped, and it is placed symmetrically in the jaws, that is, in such a way that it projects equally on both sides of the jaws. A strip four inches in width is often used between jaws one inch wide.

The relative merits of these two methods of test can be judged only after both have been tried with a wide variety of materials. It is generally recognized that the strip method gives the more accurate and reliable results but that the grab test is faster and easier to carry out. The attainment of reliable results in a grab test depends on the perfect alignment of the yarns in the jaws of the machine, so that the same set of yarns is gripped by the upper and the lower jaws. It is often very difficult to obtain this with fabrics having fine and closely woven yarns or where a nap makes it difficult to distinguish the yarns. The absence of such difficulty in testing by the ravelled strip method probably explains why more consistent results are obtained with it.

Other reasons have been advanced in favour of the strip test, for instance, it has been claimed that<sup>1</sup> "strip test results are directly proportional to the number of yarns in the width and therefore are a good test of the component yarns, grab test results do not show as good a relationship between strength and number of yarns gripped."

This is not quite true. In the first place, the breaking strength given in the strip test is not necessarily proportional to the number of yarns. An investigation by Pickles<sup>2</sup> showed that increasing the number of picks from



26 to 45, a 73 per cent increase, doubled the weft strength with one particular warp and more than doubled it with another warp. Moreover, it will be shown that for any one type of fabric, the results of the grab tests and those of the strip tests are directly related, so that any effect resulting from the increase of yarns will be reflected as well in the grab test as in the strip test.

Several investigators have compared results obtained by means of the grab test with those by the strip test, but the value of these comparisons has been largely nullified by the fact that insufficient consideration was given to the accuracy of the results, or that too small a number of fabrics was studied or that it was attempted to obtain generalizations that were too broad.

In view of the preference in some laboratories for the strip test and in others for the grab test, it would be very desirable to have a clear understanding of the possible relation between the results obtained by these two methods.

Schiefer and Taft<sup>3</sup> have studied the breaking strength of plain-weave and basket-weave fabrics as determined by the strip and grab methods. However, the main object of their investigation was not a comparison of these methods but rather a study of the effect of varying the twist of the yarns on fabric strength. Their published results do not lend themselves to the examination of the relation between the results of the two methods, since there is no indication of the accuracy of the results and in a few cases there is evidence that those obtained with the grab test are too low or the strip test results are too high. Lewis<sup>4</sup> made a study of the results obtained by means of the grab test and the strip test on a wide variety of fabrics, but too few samples of any one type were studied, his results were based on only three to five determinations for each particular fabric, and the construction of the fabrics was not given. Examination of the figures given show that some of the determinations must have been subject to large errors.

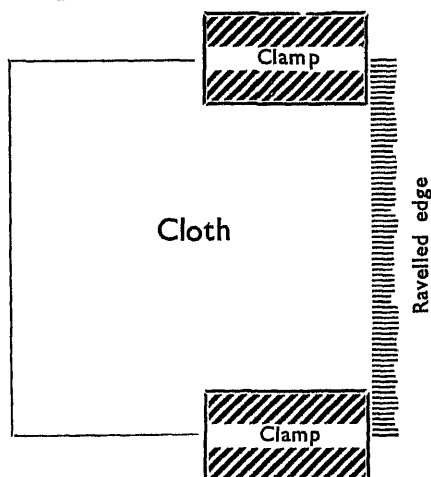
A definite attempt to correlate the results of strip tests with those of grab tests was made by Mereness<sup>5</sup>, but the actual figures from which the relations were calculated are not given, and it is difficult, therefore, to judge the accuracy of the results, although "correlation precision" is given. Mereness raised some doubt regarding the validity of the formulae proposed, owing to the "large percentages of the results falling outside the limits of reasonable agreement."

Gill<sup>6</sup> made a comparison of the two methods of test from the point of view of accuracy and time required to carry out the test. Nevertheless, on the basis of previous results and the results reported, he is of the opinion that the ratio of grab strength to strip strength is one that must be determined for each lot of fabric.

The purpose of this paper is to present additional results in regard to the relation between the grab test and strip test results and to propose a new test method possessing the advantages of the strip and grab methods.

The new test was introduced in the National Research Laboratories, Ottawa, by Mr. C. H. Bayley, and it has been called tentatively the "half-grab" test. It consists in taking a strip of cloth two inches wide and ravelling only one side of it by removing a few yarns so as to leave a well-defined edge and protruding cross-yarns as in the ordinary strip test. The strip is placed in the test machine fitted with jaws one inch wide so that

the ravelled edge is in line with one side of the jaws, as illustrated. On the other side, the strip will extend beyond the jaws for about one inch.



The advantages claimed for this method are that less material is required than for the grab test, perfect alignment of the yarns in the jaws is possible, thus increasing the reliability and accuracy of the results, and at the same time the preparation of the sample involves less work than for the strip test, since only one side is ravelled and no measurement of width is necessary.

### RESULTS

#### Time Required for Tests

A determination of the time required to carry out the three types of tests gave the following results. In order that these could be compared with those given by Gill<sup>6</sup>, a cotton anplane cloth of similar construction was used. Twenty determinations\* were carried out in each of the warp and weft directions, and the total time required was divided by 40 to obtain the mean time per test.

Time required per test (min.)	Grab	Half-grab	Strip
To prepare sample . .	0 54	48	0 89
To break sample ..	0 44	47	43
Total time	0 98	95	1 32

The observed total times for the grab and strip tests are appreciably lower than those reported by Gill. It should be noted that no particular precautions were taken in inserting the grab test pieces in the jaws of the machine, except that a pencil mark had been drawn in the centre of the strip to aid in placing the strip centrally in the jaws, otherwise the time required to break the sample would have been somewhat longer. These results show that the half-grab test is carried out as rapidly if not more rapidly than the grab test. The advantages over the strip test in this respect is evident, and for matted or milled fabrics the difference would undoubtedly have been still greater. The use of the grab test for milled fabrics or fabrics with a pile that renders the yarns undistinguishable is out of the question.

\* All strip test results reported in this paper were for strips ravelled down to 1 inch width and 3 inches between clamps. Grab tests were carried out with clamps 1 inch wide and 3 inches apart, on piece 4 inches wide.

**Variability and Accuracy**

There is no direct method by which one may judge the accuracy of breaking-strength tests. The only means at our disposal is to carry out a large number of determinations and from the standard deviation calculate the standard error or probable error. This was done with a number of cotton muslins, flannelettes, and with some wool serges and flannels, most of which were tested for breaking strength by the three methods. In actual practice one is more interested in absolute error than in relative error, however,

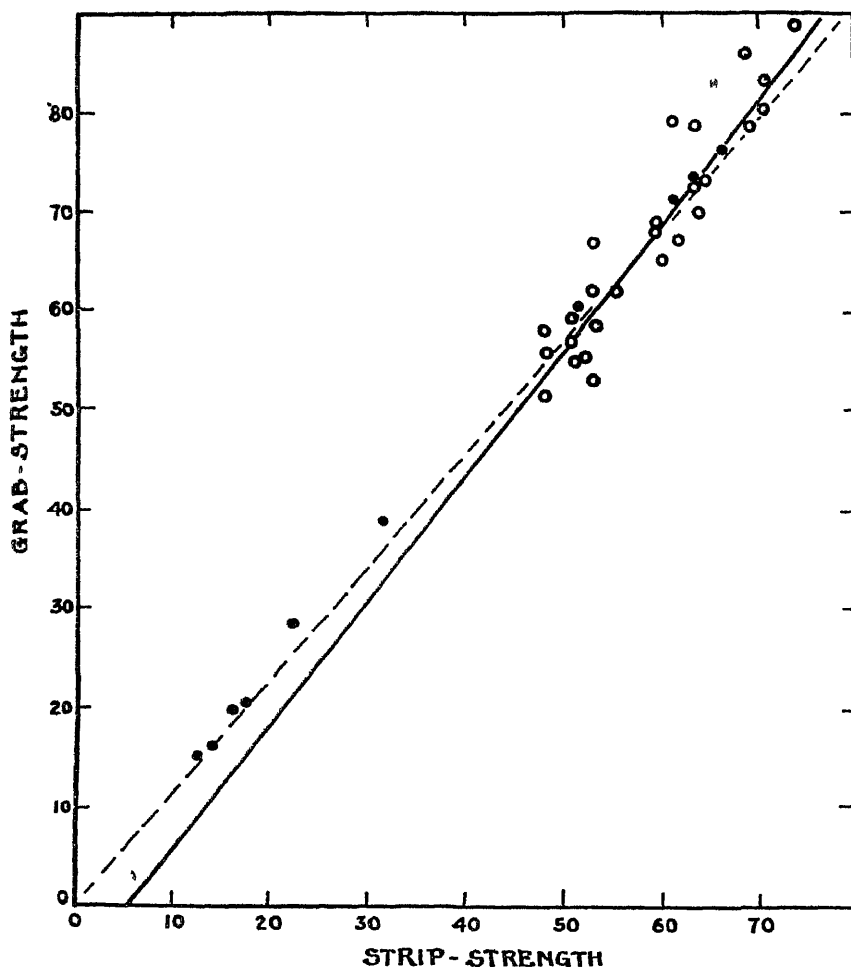


Fig 1 Strip-Grab relationship for bleached cotton muslins (warp only).

○ = Various muslins

● = Muslin with different degrees of chemical damage

since the breaking strength noted depends on the method employed, the coefficient of variation—the standard variation expressed as a percentage of the breaking strength—has been used for comparison. The results are summarized in Table I.

Table I  
Mean Coefficient of Variation for Various Fabrics

Type of fabric	No of samples	Strip method		Half-grab method		Grab method	
		Warp	Weft	Warp	Weft	Warp	Weft
Flannels ..	16	3.9	4.9	—	—	4.4	5.4
Serges . .	2	4.5	4.3	3.1	3.6	4.0	5.0
Flannels ...	3	3.6	6.2	3.3	3.6	4.3	3.7
Cotton muslin	8	5.0	—	5.0	—	5.4	—
Cotton muslin ...	*11	5.4	—	5.0	—	4.9	—
Bleached muslin	23	4.6	6.0	4.1	4.8	5.0	5.4
Grey muslin	25	4.7	5.5	3.8	4.7	5.0	5.7
Bleached flannelette	17	5.2	10.7	5.1	11.6	4.8	12.1
Grey flannelette	13	3.7	11.4	3.3	12.8	4.7	12.5
Tarantulle . ...	5	4.4	5.5	4.0	4.9	4.5	5.2

\* These samples were muslins of a construction similar to that of the previous set, but which had been deliberately damaged by treatment with sodium hypochlorite.

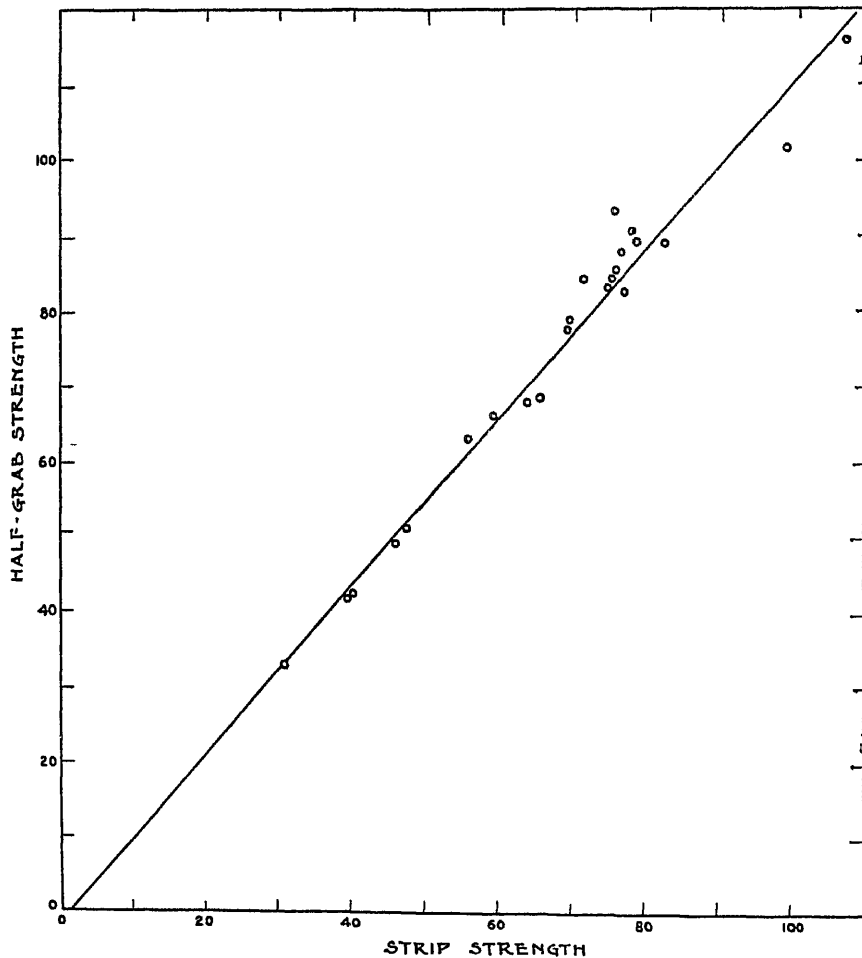


Fig 2, Strip—Half-grab relationship for grey cotton muslins

For each sample, ten specimens in the warp and ten in the weft directions were tested, except for the two serges, of which thirty specimens were tested. The standard deviation was calculated for each set of observations,

whence the coefficient of variation and then the mean of these coefficients for each particular type of material. These results show that, not only is the strip test more accurate on the whole than the grab test, as was expected, but that the half-grab test yields results that are even more reliable. Only in one case was the coefficient of variation lowest in the grab test, and this

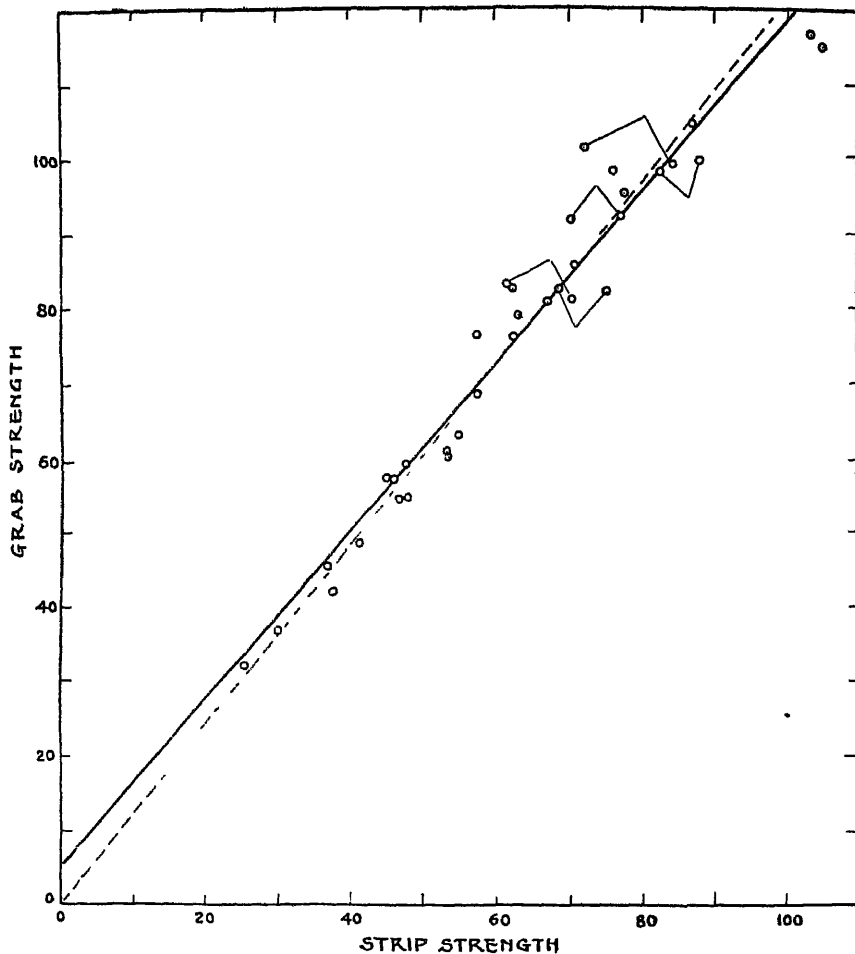


Fig 3 Strip—Grab relationship for bleached cotton muslins (weft only)

was due entirely to a very low figure for one of the samples. Had the standard deviations been used for the comparison, the strip and half-grab methods, particularly the latter, would have been shown in even a better light.

#### Relation Between the Results of the Three Methods

Assuming that a direct relation exists between the breaking strength results obtained by means of the strip method and those by any one of the other two methods, the correlation was worked out by statistical methods by making use of the equation  $Y = a + b(x - \bar{x})$  where  $x$  represents the breaking strength obtained by the strip method ( $S$ ), and  $Y$  the breaking strength obtained by either the half-grab ( $HG$ ) or the grab ( $G$ ) method, depending on whether the  $S$ - $HG$  relation or the  $S$ - $G$  relation was being

studied. In other words, a straight regression line fitted from the two statistics,  $a$  and  $b$ , was assumed to represent the relation between the breaking strength results. This assumption was made, of course, only after the observations had been plotted and it had been noted that they lay fairly close to a straight line.

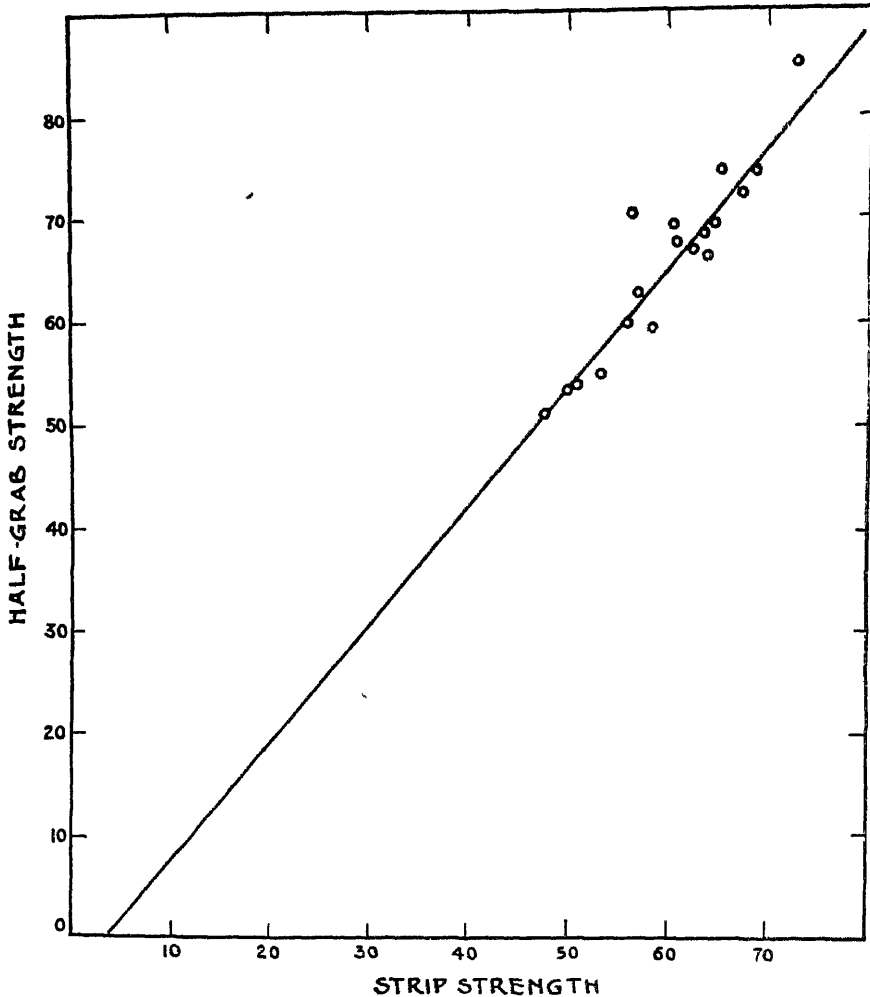


Fig. 4 Strip—Half-grab relationship for grey muslins (waip only)

$\bar{x}$  is the mean of the  $x$  values,  $a = \bar{y}$  or the mean of the  $y$  values

$$\text{and } b = \frac{\sum \{y(x - \bar{x})\}}{\sum (x - \bar{x})^2}$$

If  $\sigma^2$  is the variance of  $y$  for any value of  $x$

$$\sigma^2 = \frac{\sum (y - \bar{y})^2}{n - 2}, \text{ where } n \text{ is the number of observations}$$

and the variance of  $b$  is given by  $\frac{\sigma^2}{\sum (x - \bar{x})^2}$

$$R, \text{ the correlation coefficient} = \frac{\sum (x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2 \sum (y - \bar{y})^2}}$$

Figures 1 to 6 represent the observations noted with a number of cotton sheetings and flannelettes, and the lines drawn through them are the regression lines obtained by calculation. Similar graphs were obtained for S-G and S-HG relations not included in Figures 1 to 6

Table II is a summary of the results of the calculations and Table III is an example of the calculations in which use was made of the strength results obtained on the weft of the bleached sheetings

Table II

		$R$	$\bar{y}/\bar{x}$	$b$	Standard error of $b$	$b - (\bar{y}/\bar{x})$
<b>STRIP-GRAB RELATIONSHIP</b>						
Grey sheeting .	{ Warp	0.858	1.153	1.275	0.159	0.122
	{ Weft	0.988	1.174	1.228	0.039	0.054
Bleached sheeting . . .	{ Warp	0.971	1.143	1.273	0.097	0.130
	{ Weft	0.974	1.209	1.134	0.046	-0.075
All results .		0.964	1.172	1.198	0.031	0.026
Damaged cotton . . .		—	1.181	1.114	0.013	-0.067
<b>STRIP-HALF-GRAB RELATIONSHIP</b>						
Grey sheeting . . .	{ Warp	0.929	1.089	1.161	0.099	0.072
	{ Weft	0.985	1.107	1.127	0.042	0.020
Bleached sheeting . . .	{ Warp	0.920	1.099	1.179	0.062	0.080
	{ Weft	0.974	1.147	1.078	0.054	-0.069
All results .		0.973	1.111	1.117	0.027	0.006
Damaged cotton . . .		—	1.113	1.083	0.020	-0.030
<b>STRIP-GRAB RELATIONSHIP</b>						
Grey flannelette .. .	{ Warp	0.982	1.066	1.230	0.070	0.164
	{ Weft	0.990	1.125	1.108	0.047	-0.017
Bleached flannelette .. .	{ Warp	0.994	1.103	1.308	0.037	0.205
	{ Weft	0.944	1.172	1.249	0.110	0.077
All results . . . . .		0.985	1.110	1.096	0.025	-0.014
<b>STRIP-HALF-GRAB RELATIONSHIP</b>						
Grey flannelette . . .	{ Warp	0.994	1.035	1.102	0.036	0.067
	{ Weft	0.984	1.147	1.110	0.056	-0.037
Bleached flannelette . . .	{ Warp	0.991	1.070	1.270	0.043	0.200
	{ Weft	0.929	1.138	1.200	0.120	0.062
All results . . . . .		0.982	1.087	1.062	0.026	-0.025

Table III  
Example of Calculations: Weft Strength of Bleached Muslins  
Strip-Grab Relationship  
(Strength is given in pounds)

Strip	Grab	Strip	Grab	Strip	Grab	Strip	Grab
25.2	32.3	47.9	54.5	62.8	79.0	77.0	92.3
29.9	36.7	53.1	60.9	67.0	80.9	77.5	95.2
36.8	45.3	53.4	60.0	(3)68.5	82.5	(4)82.5	98.2
37.5	42.0	54.7	63.3	(1)70.4	81.1	(2)84.4	99.2
41.1	48.5	57.2	68.5	70.4	91.6	(5)87.0	104.6
44.7	57.2	57.2	76.5	(2)70.7	85.6	(4)87.8	99.6
45.9	57.1	*(1)61.4	83.3	72.0	101.2	(5)103.1	116.6
46.6	54.3	62.2	82.6	(3)75.1	82.1	(5)105.0	115.0
47.6	59.0	62.3	76.4	76.0	98.3		
						$n\bar{x} = 2201.9$	$n\bar{y} = 2661.4$

\* Results bearing the same designations were obtained on samples from the same quality sheeting but obtained from different sources.

Number of tests,  $n=35$

$$\bar{x}=62.911429 \quad \bar{y}=76.040000$$

$$\bar{x}^2=3957.8479 \quad \bar{y}^2=5782.0816$$

$$\Sigma x^2=150975.63 \quad n\bar{x}^2=138524.67$$

$$\Sigma y^2=219229.34 \quad n\bar{y}^2=202372.86$$

$$\Sigma xy=181546.38 \quad n\bar{x}\bar{y}=167432.48$$

$$\Sigma(x-\bar{x})^2=12450.96$$

$$\Sigma(y-\bar{y})^2=16856.48$$

$$\Sigma(xy) - n\bar{x}\bar{y}=14113.90$$

$$b = \frac{\Sigma(xy) - n\bar{x}\bar{y}}{\Sigma(x-\bar{x})^2} = 1.133559$$

$$\sigma^2 = \frac{\Sigma(y-\bar{y})^2}{n-2} = \frac{\Sigma y^2 - n\bar{y}^2 - b \{ \Sigma(xy) - n\bar{x}\bar{y} \}}{33}$$

$$= 25.986$$

$$\sigma = 5.098$$

$$\text{Variance of } b = \frac{\sigma^2}{\Sigma(x-\bar{x})^2} = 0.002087$$

$$\text{Standard error of } b = 0.046$$

$$\text{Slope } \bar{y}/\bar{x} = 1.209$$

$$R = \frac{\Sigma(x-\bar{x})(y-\bar{y})}{\sqrt{\Sigma(x-\bar{x})^2 \Sigma(y-\bar{y})^2}} = 0.974$$

#### DISCUSSION

From a consideration of the figures given in Table II there can be no doubt that the results obtained by means of the strip method are highly correlated to those obtained by either of the other methods since the value of  $R$  in all cases is very nearly unity

The values of  $b$  represent the slope of the regression lines and the ratios  $\bar{y}/\bar{x}$  represent the slope of the lines passing through the origin and the mean values of  $x$  and  $y$  or their centre of gravity

There seems to be no *a priori* reason why the line representing the relation between two sets of results should not pass through the origin.

It will be noted in the curves shown that the regression lines cross the  $x$ -axis a short distance from the origin in some, while in others they intercept the  $y$ -axis. However, examination of the figures will show that this occurs only where there are no observations near the origin. Where low breaking strengths were noted (weft of the flannelettes, Figs 5 and 6, and damaged cotton, Fig 1), or where the observations are spread over a wide range so as to define more closely the direction of the line (Fig 2), the line through the observed points passes through, or very close to, the origin. In the other cases, a small error in the slope is sufficient to explain the deviation from the line through the origin

To Figure 5 have been added a few results obtained with plain woven fabrics other than cotton. These results lie very close to the line passing through the origin

The value of the intercept can have no physical meaning because it can signify only that the material having a certain strength when tested by one method has none when tested according to the other method. One might interpret the  $y$  intercept ( $x=0$ ) as representing a *constant* increment



to the strip test that has to be added to represent the contributing factor of the additional threads of the half-grab and grab test pieces, but, if that were so, a curved line would be obtained for the relation. Moreover, only in a few cases is  $y_0$  positive. The conclusion may therefore be drawn that the values of  $y_0$  or  $x_0$  are purely the result of experimental error. That

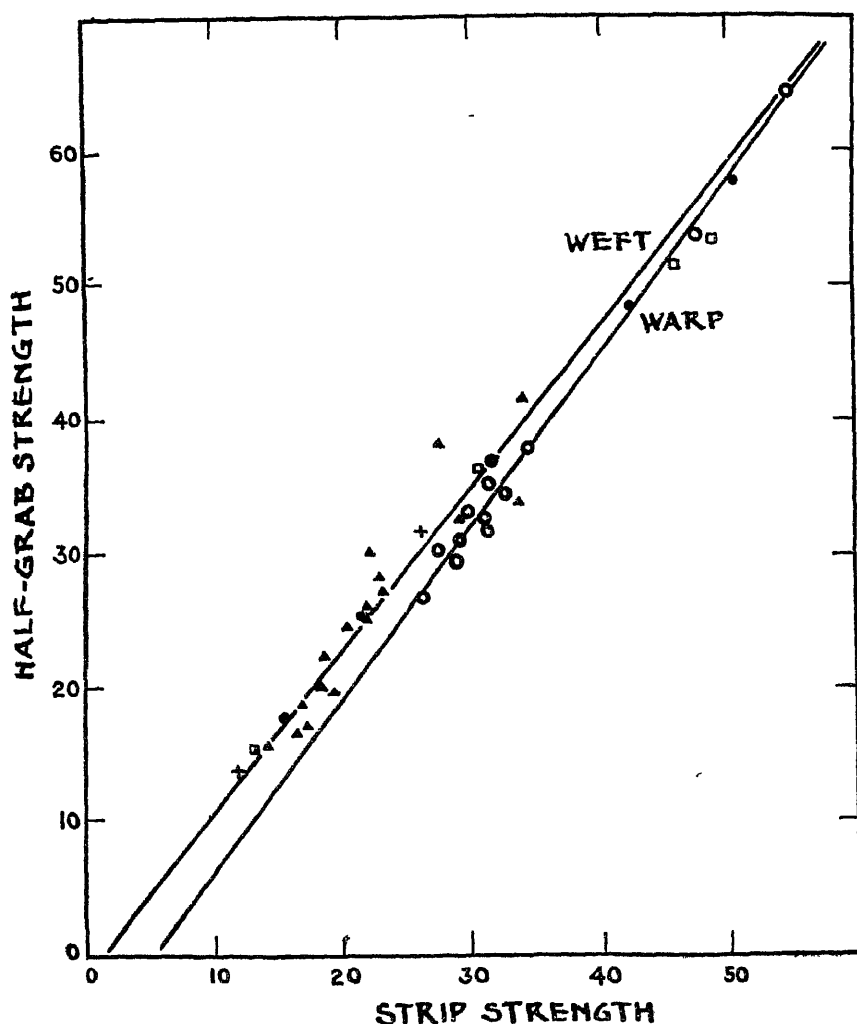


Fig 5 Strip—Half-grab relationship for bleached flannelettes and few other fabrics (warp of latter only)

- = Flannelette warp
- ▲ = Flannelette weft
- + = Fibro + cotton mixture
- = Celanese
- = Viscose
- = Silk

this is so is further confirmed by a comparison of the values of  $b$  with those of  $\bar{y}/\bar{x}$ , Table II. Their differences are given in the table, together with the standard error of  $b$ . It will be noted that with the possible exception of the results for the warp of the bleached flannelettes, the difference  $b - \bar{y}/\bar{x}$

is not significant. This is corroborated by application of the  $t$ - $P$  test for significance. The test of significance was also applied between various pairs of  $b$ , for example, between the values of  $b$  for warp and those for the weft, or between the values for the bleached and those for the grey muslins, etc., and in only one case was the difference possibly significant, namely, the difference between the value of  $b$  for the warp of the bleached flannelettes and that of the weft of the grey flannelettes in the grab-strip relation

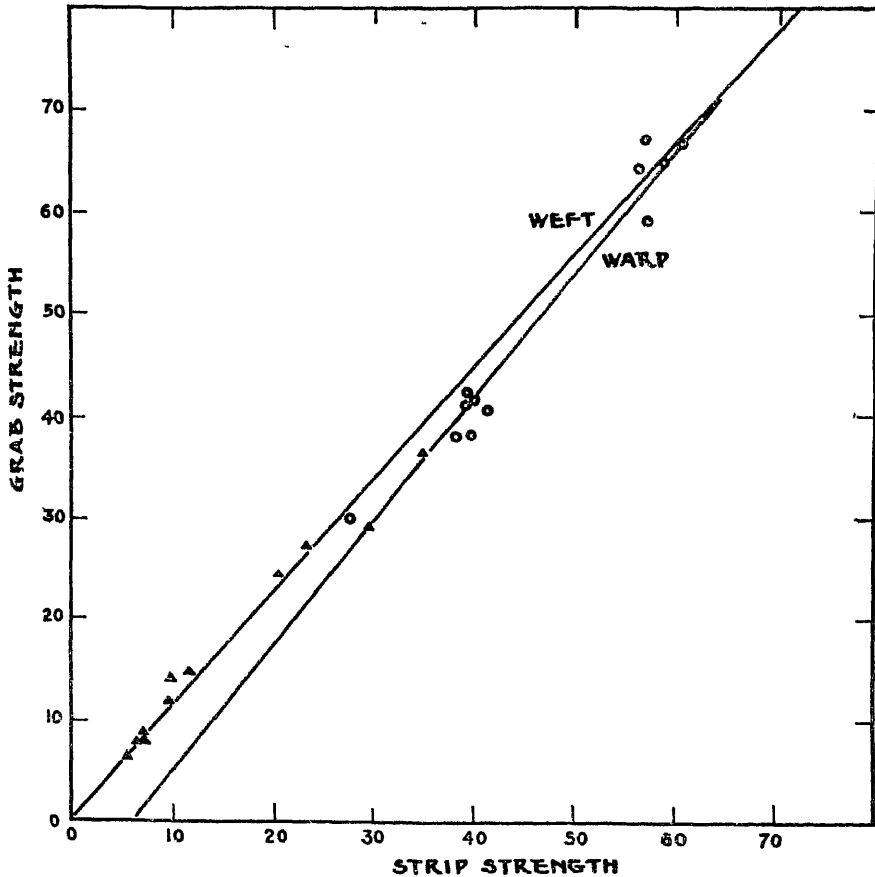


Fig 6 Strip—Grab relationship for grey flannelettes

▲ = Weft  
○ = Warp

For this reason one may be justified in grouping all the results together in obtaining a mean slope for the relation studies, although normally this would not be necessary since for specification purposes, for which the relations discussed are of importance, the interest would be only in one particular type of fabric, and any variation for this class of fabric would be smaller than that noted in the present investigation

Although statistical methods show no significant difference between the various slopes noted, examination of the results given in Table II indicates a constant difference between the results for warp and weft or between those for sheetings and the flannelettes

That such a difference should exist is to be expected. It is evident that the higher results of the grab or half-grab tests are due to the additional side threads that exert their action through the bonding with the cross threads between the clamps as well as in the clamps themselves. This bonding effect apparently varies in the warp and weft directions, although the way in which this transmission of force acts is not a simple one. For example, no correlation has been found between the ratio grab strength to strip strength and the closeness of the weave or number of threads per inch, which one would expect to affect the ratio.

Experiments will be carried out with a view to determining how the transfer of this additional force takes place.

The bonding effect also varies, as is to be expected, with the type of cloth. The difference between the sheetings and flannelettes has already been mentioned, the reinforcing effect being less in the flannelettes than in the muslins. On the other hand, the bonding effect would be expected to be high in woollen fabrics, particularly if they have been milled or fulled. This is well shown by the figures given in Table IV, which represent the results obtained with a few fabrics of that type.

It will be seen that the ratios are fairly constant for any one type of fabric but that there is a variation between one type and another.

**Table IV**  
**Ratios of breaking strengths determined by the strip, half grab and grab methods for a number of woollen fabrics**  
The strip breaking strength is taken as unity

	Half-grab		Grab	
	Warp	Weft	Warp	Weft
Serge A	1.10	1.18	1.35	1.40
„ B	1.23	1.21	1.52	1.40
„ C	1.23	1.19	1.64	1.61
„ D	1.33	1.32	1.53	1.58
„ E	1.41	1.51	1.76	2.07
„ F	1.43	1.63	1.82	2.10
Beaver	1.26	1.39	1.43	1.77
Flannel A	1.28	1.31	1.61	1.74
„ B	1.32	1.30	1.62	1.65
„ C	1.34	1.41	1.59	1.78
„ D	—	—	1.52	1.56
„ E	—	—	1.55	1.65
„ F	—	—	1.51	1.61
„ G	—	—	1.45	1.62
„ H	—	—	1.45	1.50
„ I	—	—	1.45	1.48
„ J	—	—	1.54	1.56
„ K	—	—	1.34	1.43
„ L	—	—	1.12	1.41
„ M	—	—	1.14	1.38
„ N	—	—	1.13	1.11
„ O	—	—	1.13	1.09

Serges A, B, C and D were worsted serges, and E and F woollen serges.

Flannels A, B, C were of one type.

„ D, E, F, G were of one type.

„ H, I, J, K were of one type.

„ L, M had a cotton warp.

„ N, O contained about 50 per cent cotton in both warp and weft.

#### REFERENCES

- <sup>1</sup> J. H. Skinkle *American Dyestuff Reporter*, 1938, 27, 161.
- <sup>2</sup> Pickles *Journ. Textile Science*, 1931, 4, 36.
- <sup>3</sup> Schiefer and Taft *J. Res. National Bureau of Standards, U. S. A.*, 1936, 16, 131.
- <sup>4</sup> Lewis *Proceedings American Society for Testing Materials*, 1916, Pt. I, 366.
- <sup>5</sup> Mereness *Textile Research*, 1938, 8, 165.
- <sup>6</sup> Gill *Textile Research*, 1939, 9, 141.

Received 29/4/41

## 13—ROLLER SETTINGS AND YARN STRENGTHS

By F. DUNKERLEY

(Ministry of Agriculture, Egypt)

*Copyright by the Textile Institute*

## INTRODUCTION AND SUMMARY

The experimental evidence presented in this paper is drawn from the results of over 1,000 spinning tests, conducted equally on 18 different types of Egyptian cottons, and from the breaking of more than 20,000 leas.

The objects were:—

- (a) To find out the effects on resulting yarn strengths of changes in roller settings at slubber, intermediate, rover, and ring frames separately
- (b) The settings for maximum strength having been ascertained, to find out how these maximum settings could be related to staple length
- (c) Comparing Casablancas Apron systems with three-line and light-middle-top-roller systems, using the same drafts and speeds for both, to find out by how much did these roller systems differ in sensitivity to changes in roller settings distances

Results obtained may be stated as follows:—

- (a) Small changes in roller settings have little effects on yarn strength, especially when roller settings are made wider than the optimum, but if errors in settings are made at each stage, the cumulative effect may be quite appreciable.
- (b) Staple length as normally understood can be used as a guide to roller settings on the speed frames three-line roller systems. In the experiments here recorded, little loss in resulting yarn strength was found when the slubber and intermediate, using weighted three-line roller systems, had settings such that the distance between front and middle lines roller nips was equal to staple length plus  $\frac{4}{8}$  in., the equivalent setting for the rover, using a self-weighted three-line roller system, was equal to staple length minus  $\frac{2}{8}$  in.
- (c) The difference in sensitivity at each stage was found to be slight when considering settings up to  $\frac{1}{8}$  in. wider than the optimum, but the weighted three-line systems on slubber and intermediate showed serious losses in resulting yarn strengths for the weaker samples when the settings were very close; the fall in strength at close settings was absent from the Casablancas systems. In this sense, the weighted three-line systems were more sensitive to changes in roller setting distances than were the corresponding Casablancas systems.

In our spinning test technique as previously described by Hancock<sup>1</sup>, the Casablancas systems and the three-line systems on all three speed frames are worked at the low draft of 5 in each case. A discussion of the relative top strengths of yarns processed on the two systems, with particular reference to the use of Casablancas systems on speed frames for speedy testing technique will be the subject of another paper<sup>2</sup>.

Table I shows the samples and their more important measurable characters, Table II is a complete list of the settings adopted.

**Table I**  
**Cottons and Characters**

Sample	Reference Letter	*Staple Length 1/32" units	Mean Length inches	Hair Weight
<b>SHORTER STAPLES GROUP.</b>				
Zagora FGF	A	40	0 90	176
Zagora FG	B	41	0 96	185
Zagora FG Combed	C	41	1 04	186
Zagora FG Double-combed	D	41	1 08	185
Uppers FGF	E	40	0 93	172
Uppers FG Combed	F	40	0 97	179
<b>MEDIUM STAPLES GROUP</b>				
Giza 12 FG	G	44	1 01	147
Giza 12 FG Double-Combed	H	48	1 22	142
Giza 7 FG	J	45	1 07	148
Sakel FGF	K	43	1 00	130
Sakel FGF	L	42	0 95	128
Sakel FGF Combed	M	46	1 09	128
<b>LONG STAPLES GROUP</b>				
Sakel Extra	N	51	1 20	123
Sakha 4 FG Combed	O	50	1 20	122
Giza 26 FGF	P	51	1 07	112
Giza 26 FG Combed	Q	49	1 20	128
Giza 26 FG Combed	R	53	1 30	123
<b>MIXING 50-50</b>				
Uppers FG	S	51	1.12	127
Sakha 4 FG				

Giza 12 = Wafeer

Giza 26 = Malaki

\*Staple length measured from the "half-fall" of the Balls Sorter Diagram

**Table II**  
**Relation of Front-to-Middle and Middle-to-Back Roller Settings used for the Different Experiments**

All settings given in 1/32" units, Front-to-Middle first

THREE-LINE SYSTEMS				CASABLANCAS SYSTEMS			
Slubber	Inter	Rover	Ring	Slubber	Inter	Rover	Ring
38-55	38-55	38-46	29-45	67-47	67-47	62-47	57-52
42-55	42-55	38-52	29-51		71-47	66-48	61-56B
46-55	46-55	42-56	31-45A	75-50	75-50	70-53	
50-55	50-55	46-55	31-47				
54-58	54-58	46-60	35-51				
58-62	58-62	50-59					
62-66	62-66	50-64					
66-70	66-70	54-63					
66-74	66-74	54-69					
		58-67					
		62-71					
		66-74					

A—was used for comparison with Casablanca

B—was used for comparison with LMTR

Where two Middle-to-Back settings are given for one Middle-to-Front, adjustments were made for staple length to conform with the machinery maker's recommended settings, details on Figures 3 to 5A

### A. SPEED FRAMES WITH THREE-LINE SYSTEMS

#### A1. Experimental Procedure

For each cotton a range of five roller settings was chosen at each frame, rising in steps of  $\frac{4}{52}$  in units, to straddle the correct setting, which was known approximately from previous experience. Subsequent treatments

for all the five lots of material from each frame were identical, with any inaccuracies in settings at later stages common to all, the setting associated with highest yarn strength at each stage was adopted as the optimum setting.

Results from the five slubber settings are shown in Figure 3. The roller system of the slubber is shown in Figure 2, all three lines of top rollers were weighted, back and middle lines by saddle and front line by dead weighting.

Slubbing produced from the optimum setting was used for the five intermediate frame roller settings, Figure 4. The roller system of this machine was identical with that of the slubber.

Intermediate roving produced from the optimum settings of slubber and intermediate was used for the five rover roller settings, Figure 5. The roving frame had self-weighted back and middle lines of rollers (the middle top roller weighing 350 grams), and dead weighted front line, Figure 2.

In practice, because of the wide straddle in settings adopted for the testing of the three-line systems, it was found unnecessary to test each of the cottons separately, the 18 samples were dealt with in three groups, shorter staples, medium staples, and long staples, for economy of labour. Excepting for these variations in drafting treatments, the procedure was precisely as described by Hancock.<sup>1</sup> All samples from speed frame experiments were spun on Casablancas systems at the ring frame under identical conditions, the counts being 60's ring twist.

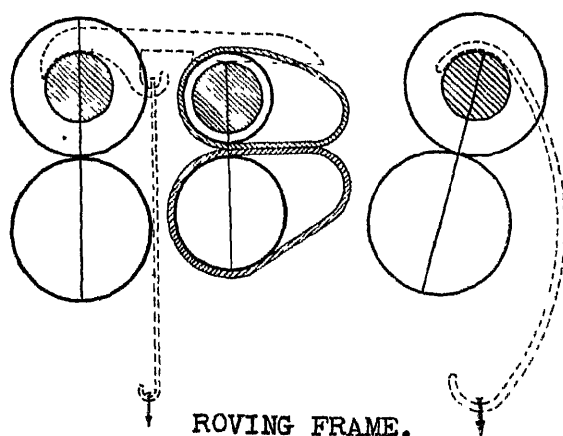
## A2. Roller Settings for Three-line Systems

Roller setting distances were measured from roller nip to roller nip, and are quoted in  $\frac{1}{8}$  in units. Settings for the three-line systems on the speed frames were based on settings recommended in a leading machinery maker's Handbook. It was found impossible to adhere strictly to the recommended settings, because the machinery maker quoted different roller diameters for various settings and staple lengths, our rollers were the same diameter for all samples and settings. Furthermore, the three-line systems were not built to allow settings so divergent as those used in these experiments. An instance of this limitation was found on both the slubber and the intermediate where the middle to back line settings could not be made closer than 55. In conformity with the recommended settings, slight changes were made where possible in the relationship between front to middle, and middle to back, line settings for the shorter, medium, and long-stapled cottons.

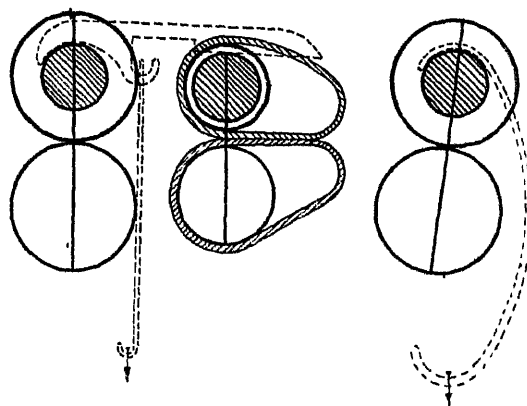
## A3 Discussion of Results for Three-line Systems

Slubber and intermediate frames, with all three lines of top rollers weighted, gave results of a similar character. In the majority of cases, there was a setting on either side of which the resulting yarn strength fell. With the shorter cottons at least, the rate of fall in yarn strength was greater with closer settings than it was with wider settings. The weaker samples lost proportionally more yarn strength than did the medium or long staples, which were the stronger samples, at the closer settings. The fall in yarn strength when the setting distance was  $\frac{1}{8}$  in wider than the optimum, for any one sample, was, in general, small. It would appear that no great losses in resulting yarn strengths would be found should roller settings be a little on the wide side on the speed frames. Where correct roller settings

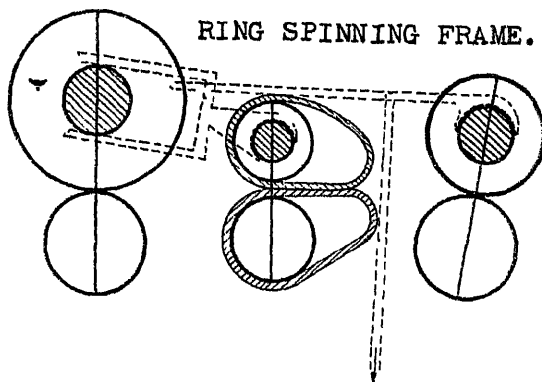
SLUBBER AND INTERMEDIATE FRAMES.



ROVING FRAME.



RING SPINNING FRAME.



Scale in inches.

Fig 1 Casablanca's Drafting Systems

were in doubt, a spinner might, with no great disadvantage, employ settings a little on the wide side when first processing a changed type of material.

The rover, using self-weighted back and middle top rollers, behaved in a quite different manner. Results from tests, including the closest possible setting, are shown in Figure 5A. With most of the shorter stapled samples, resulting yarn strengths continued to rise up to the closest possible setting, and in general falls in strength at close settings were slight. In most cases, a spinner beginning a fresh type or a changed mixing, with rover roller settings close, would be unlikely to sacrifice more than about 1 per cent of possible yarn strength, and could move out if roving breaks or yarn appearance made such a course necessary.

The setting distances producing highest yarn strengths may not be the best possible for industrial purposes. This point will be discussed in a later section of the paper.

#### A4. Staple Length and Roller Settings

For slubber and intermediate frames the curves of yarn strength from varying roller settings on the three-line systems fell on either side of an optimum setting for maximum resulting yarn strength. The rate of fall from optimum to wider settings was very small and the curves tended to be flat-topped. At setting distances equal to staple length plus  $\frac{4}{8}$  in., the yarn strength for the 18 samples was on the average within 0.5 per cent of the maximum recorded for the slubber, and within 1 per cent. of that recorded for the intermediate.

A rover roller setting distance equal to staple length minus  $\frac{2}{8}$  in. gave average resulting yarn strength only 1 per cent below the maximum recorded, but this result should be taken with some reserve because there were samples which had perhaps not reached maximum strength even at the closest setting possible.

### B. SPEED FRAMES WITH CASABLANCAS SYSTEMS

#### B1. Experimental Procedure

Alongside the three-line system preparations, a separate series of rovings was prepared at the same time, under identical drafting and speed conditions.

Two settings were used on the slubber, closest possible and  $\frac{4}{8}$  in. wider than closest possible.

Three settings on the intermediate were closest possible and two wider settings,  $\frac{4}{8}$  in. wider and  $\frac{8}{8}$  in. wider.

Three settings on the rover were closest possible, and two wider settings,  $\frac{4}{8}$  in. wider and  $\frac{8}{8}$  in. wider.

All three Casablanco systems are shown in Figure 1. Slubber and intermediate were identical, and all three systems had back and middle lines weighted by saddle and front lines dead-weighted, with tensors, size 6, throughout.

#### B2. Roller Settings for Casablanco Systems

The roller settings used were based on Spinning-Test Mill settings which had given satisfactory results for a period of over five years, in the absence of a guide to roller settings under the conditions of these experiments. The nip distance for middle to front lines greatly exceeds that of middle to back lines, but at the closest settings the fronts of the aprons were within  $\frac{1}{8}$  in. of the perimeter of the front rollers.  $\frac{4}{8}$  in. was the closest possible setting for the middle to back lines on all three speed frames.



SLUBBER AND INTERMEDIATE FRAMES.

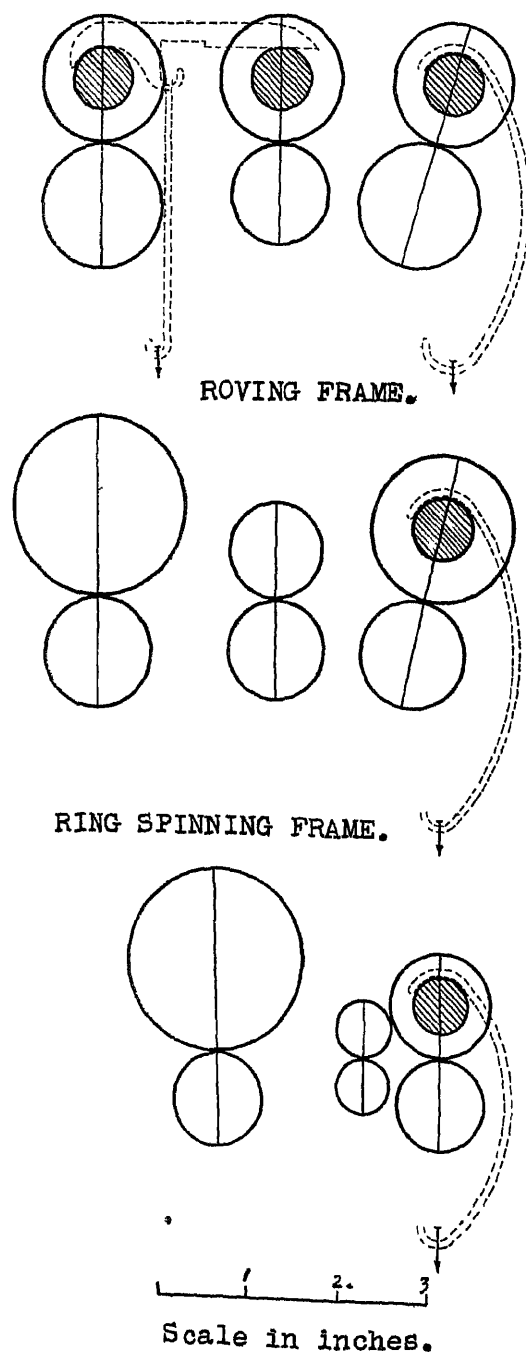


Fig. 2 Three-line Drafting Systems

**B3. Discussion of Results for Casablanca Systems**

Small changes in roller settings had little effect on resulting yarn strengths (Figure 6). But in general, the closer the setting the higher the yarn strength, on all three frames. The closest settings were the closest possible on the machines, and the settings used at each process were the same for all samples irrespective of staple length or resulting yarn strength. No crackers were

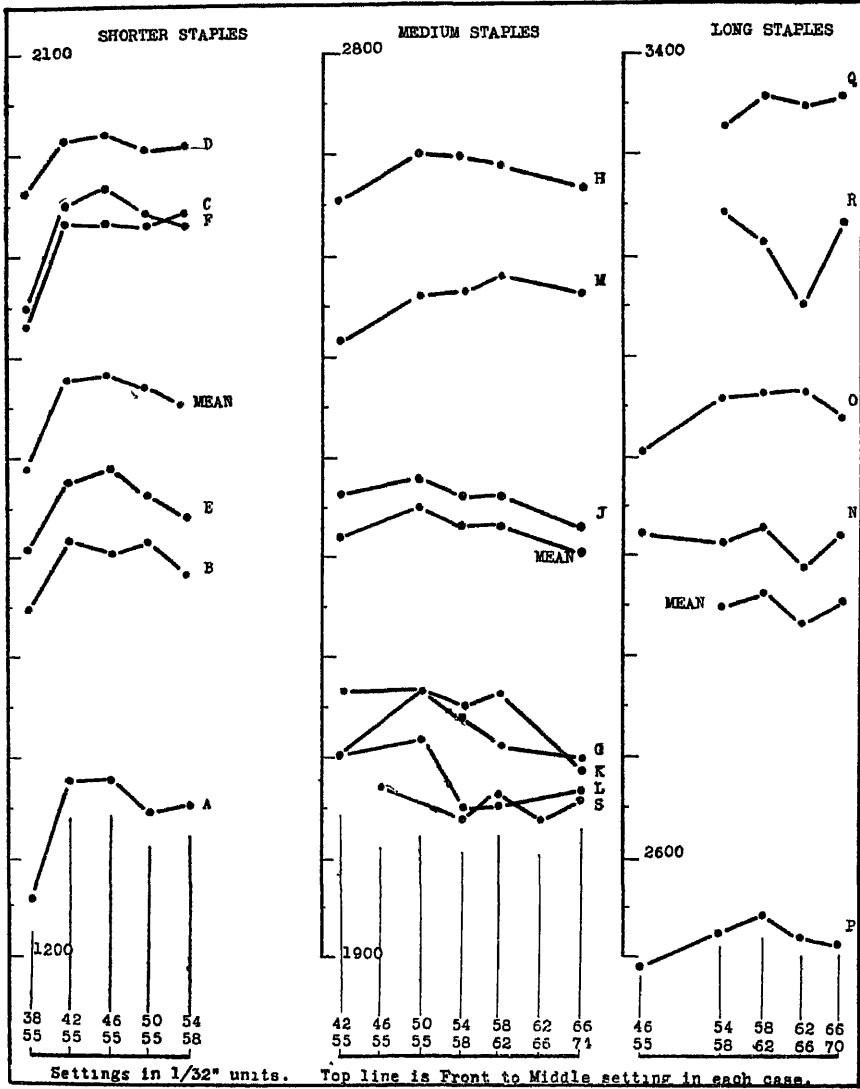


Fig. 3 Roller Settings and Yarn Strengths from Slubber Experiments.  
Three-line System

See Table I for key to reference letters

observed at any stage. The Casablanca systems produced highest yarn strengths at closest possible settings on all three machines, excepting with the longest stapled samples. A spinner, having found the best positions for his particular case, could change his cottons of mixings within the Egyptian range without changing roller settings.

### C. COMPARISON BETWEEN THREE-LINE AND CASABLANCAS SYSTEMS

#### C1. Sensitivity of the Two Systems to Roller Settings

With Casablanca systems, the shorter cottons at close settings showed none of that rapid fall in strength which characterised the three-line systems at slubber and intermediate under the same conditions. Casablanca systems

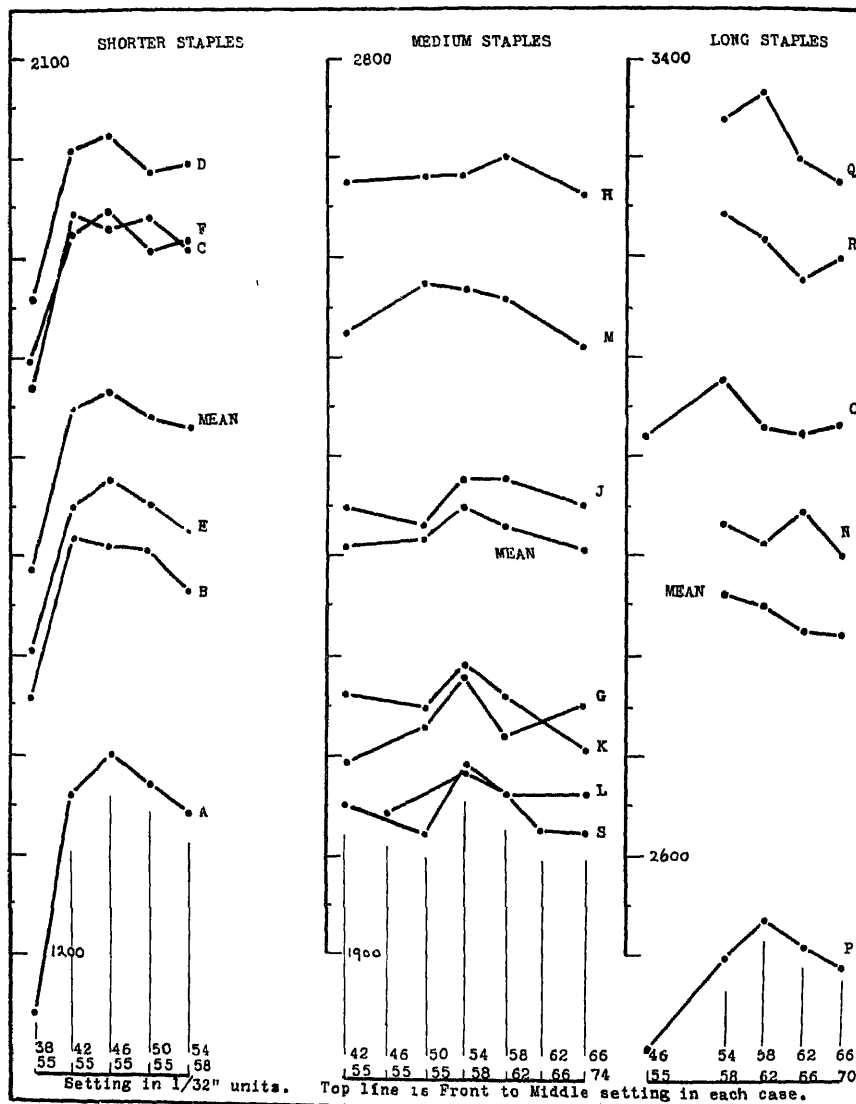


Fig. 4. Roller Settings and Yarn Strengths from Intermediate Experiments  
Three-line System  
See Table I for key to reference letters

were therefore to that extent very much less sensitive to roller settings, as regards the subsequent effect on yarns strengths, than were the three-line systems. With the longer cottons, however, such serious falls in resulting yarn strength were not found with either system at close settings, nor did

the systems differ greatly in sensitivity at settings wider than the optimum with any cottons. The average fall in resulting yarn strength at each stage for all the samples listed in Table I, when the settings were moved out one-quarter inch wider than the estimated optimum settings, were —

	Percentage fall in yarn strength		
	Slubber	Inter	Rover
Three-line ...	0.5	0.5	1.5
Casablancas	1.0	0.5	2.0

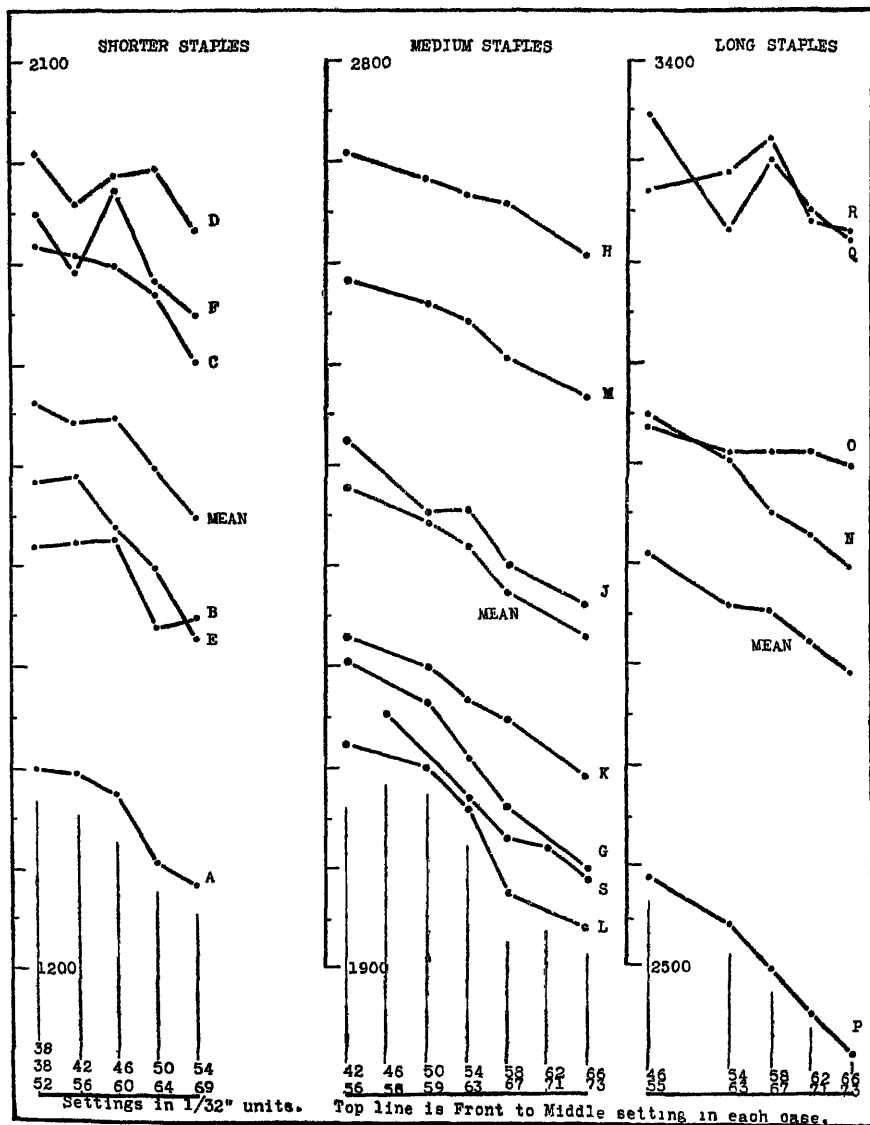


Fig 5 Roller Settings and Yarn Strengths from Rover Experiments  
Three-line System  
See Table I for key to reference letters

**C2. Higher Strengths from Casablancas-Processed Rovings.**

The experiments discussed were carried out with comparable draft and spindle speed at each speed frame. All resulting rovings were of roughly equal hank, and were spun under identical conditions into 60's ring twist yarns on a spinning frame equipped with Casablancas drafting systems. Under these conditions, the rovings from the Casablancas systems at the speed frames produced stronger yarns than did the rovings from the three-line systems at the speed frames. For all three speed frames together, gains in resulting yarn strengths of Casablancas systems over three-line systems up to 7 per cent were recorded, the average gain for the 18 samples of Table I was about  $4\frac{1}{2}$  per cent.

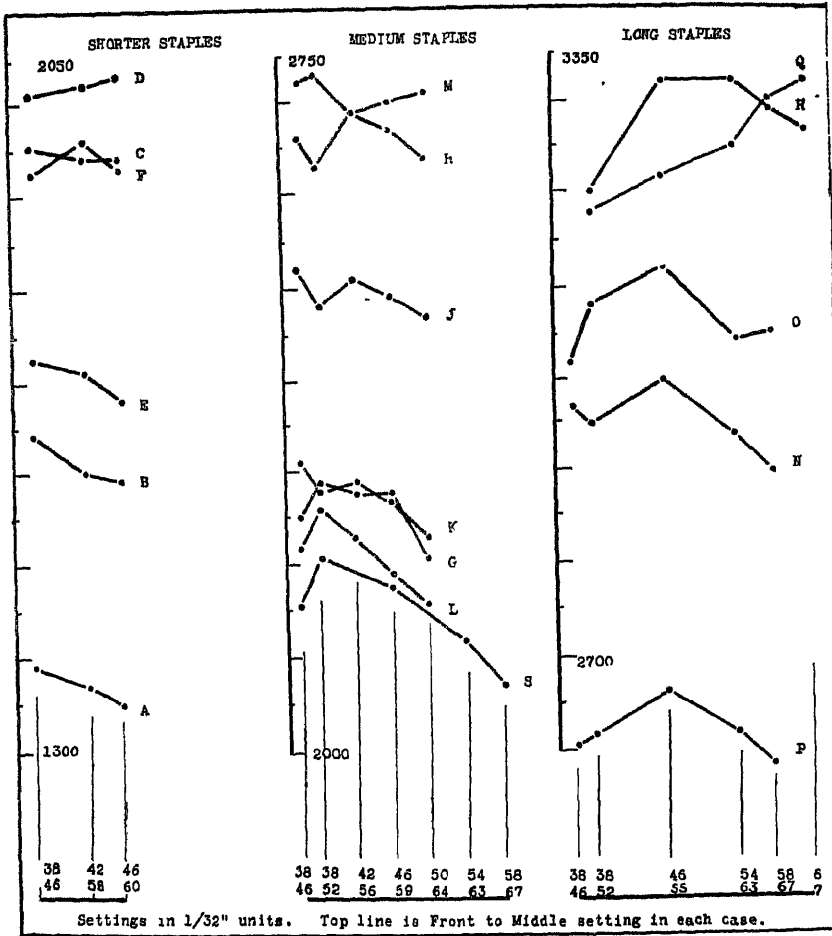


Fig 5A Yarn Strengths from closest possible settings on Rover.  
Three-line System  
See Table I for key to reference letters.

**D. RING FRAME. BOTH SYSTEMS**

**D1. Preparation of Rovings for Ring Frame Experiments**

The Light-middle-top-roller system at the ring frame was varied, using material produced under identical conditions on Casablancas systems at the speed frames, and material was similarly prepared for the comparison of the

Casablancas system with the Light-middle-top-roller system at the 111g frame.

## D2. Light Middle Top Roller System. Ring Frame

This roller system had a light-weight middle top roller weighing 85 grams. Variation of middle to back, and middle to front roller settings simultaneously, using the 18 samples of Table I, Casablancas system processed at the speed frames, under identical conditions, produced yarn strengths shown in Figure 7. Almost the whole of the samples behaved in a similar manner to changes in roller settings and Figure 7 indicates that at a setting of 29-51 the yarn strength for each sample, excluding the Giza 26 combed samples, was near to the maximum recorded. The behaviour of this Light-middle-top-

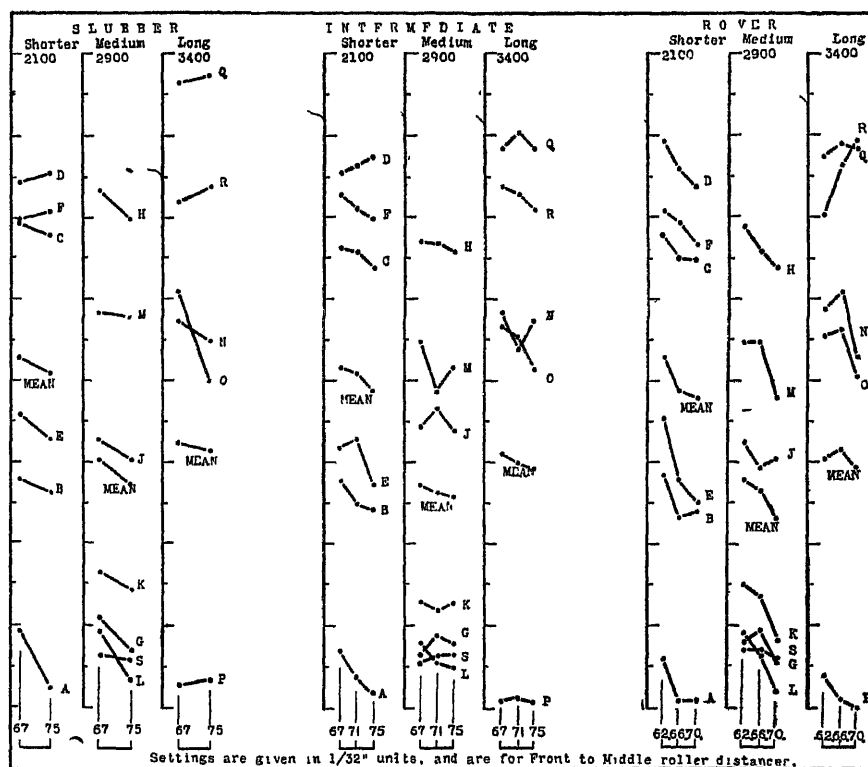


Fig. 6. Roller Settings and Yarn Strengths Speed Frames.  
Casablancas Systems

See Table I for key to reference letters

roller system approximates to that of the 10ver in that, in general, highest yarn strengths were produced when the middle to front lines had the closest possible setting on each machine. But a new phenomenon appeared, when middle to front line, and middle to back line, settings were the closest possible at the same time, yarn strengths fell. A test varying middle to back roller settings, using two samples from near to the extremes of the staple range, with front to middle line at a constant setting of 29, produced yarn strengths not very different even when the back to middle line settings were 45 and 70, but the yarn from setting 29-50 was a little stronger than

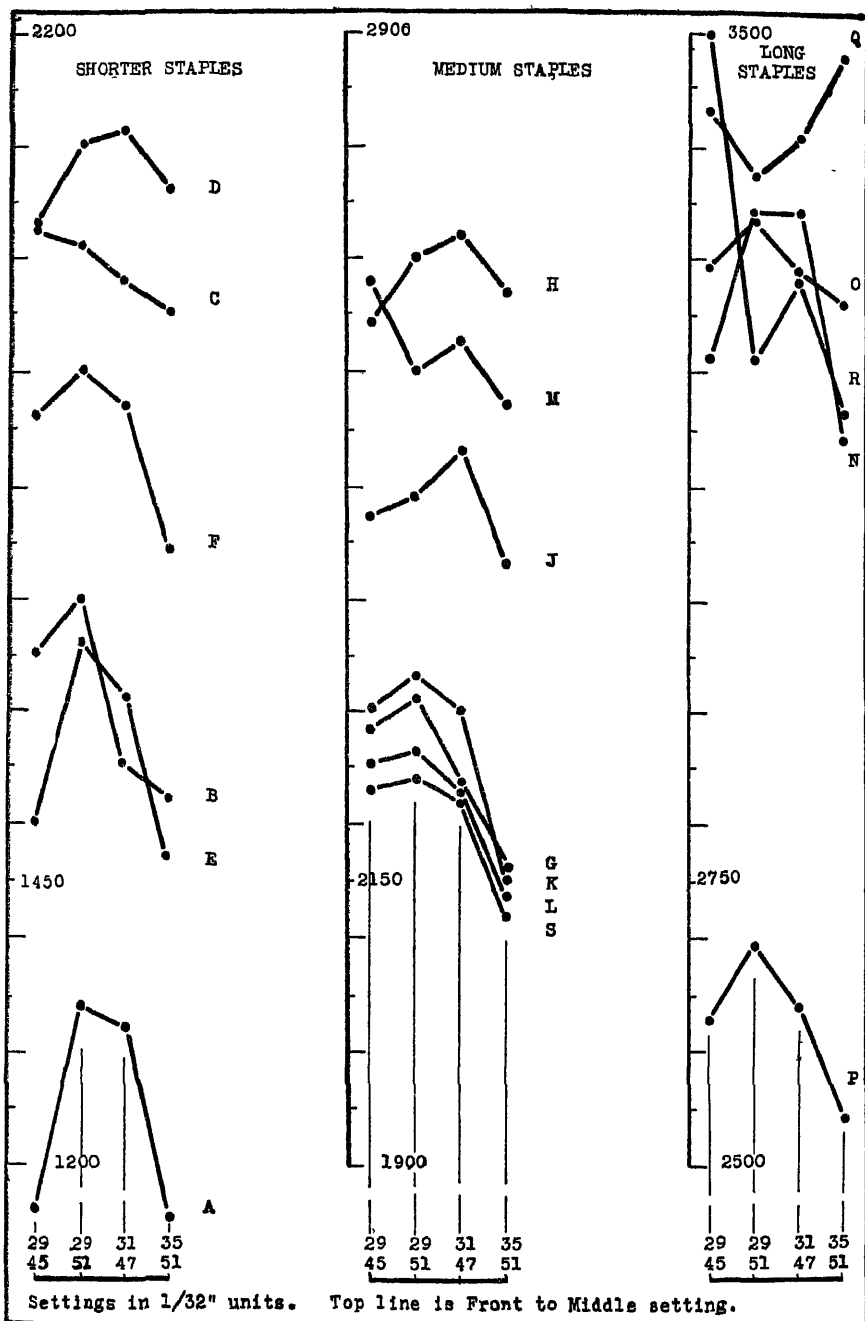


Fig. 7 Roller Settings and Yarn Strengths from Ring Frame Light Middle Top Roller System.

See Table I for key to reference letters.

that from setting 29-45, this result, so far as it goes, tends to confirm the drop in strength with closest settings previously observed

### **D3. Comparison of Casablancas System with Light-Middle-Top-Roller System. Ring Frame**

From previous experience of the spinning of high-quality, long-stapled, combed samples in the Spinning-Test Mill, it was known that the closest setting of 57-52 of Casablancas system on the spinning frame, which uses tensors of size 5, produced "crackers." For comparison with the Light-middle-top-roller system a setting of 61-56 was adopted. At this setting drafting proceeded satisfactorily for all the 18 samples, although there may have been a slight fall in the strength level of the system.

The settings adopted for the Light-middle-top-roller system were constant for all samples at 31-45. From considerations discussed in the previous section, this setting probably produced a slight fall in the strength level of the system.

The rovings used were all produced under identical conditions, using Casablancas systems at the speed frames, and were made from the samples listed in Table I. Only the effects of the two roller systems at the spinning frame at the given settings are therefore included. The spinnings were done on the same frame, one side Casablancas system, the other side Light-middle-top-roller system, at the same time, with equal draft, and the counts were 60's ring twist. Under these conditions, the Casablancas system produced yarns which were, on the average, 2.5 per cent stronger than those produced by the Light-middle-top-roller system.

## **GENERAL CONCLUSIONS**

The experimental evidence for these conclusions should be adequate, being based on seven Egyptian cotton varieties, with more than one grade in four cases, making 18 different samples. There were about 1,000 spinnings, and 24lea tests were made on each spinning.

Although the highest yarn strengths attained during these experiments were produced at certain roller settings without the appearance of "crackers" at any stage, and though such settings were found to be practicable for spinning tests, these optimum settings are not put forward as the best possible for extended running under industrial conditions. A host of considerations, beyond the scope of any testing plant, including hanks, drafts, twists, speeds, contribute to the totals of roving and yarn breaks per hour which is the controlling condition for industrial production. But the experiments repeated on an industrial scale would probably take settings either changed by a constant amount, or by an amount proportional to staple length, leaving the relative values unchanged.

A machinery maker's Handbook recommends slubber and intermediate settings, on the three-line systems, which are not very different from the optimum settings found by these experiments, though the roller diameters are changed with changing staple length. The same Handbook gives roving roller settings wider than those here found to produce highest resulting yarn strengths. No comparable data for the Light-middle-top-roller system, or for the Casablancas system, under the given conditions, was found.



Assuming the machinery maker's recommended settings to be representative of those generally used by industry, no great losses in resulting yarn strengths are likely to accrue from the adoption of those settings on three-line systems at slubber and intermediate, but, where doubt of correct settings exists, it would appear that errors of setting on the wider side would be less serious than similar errors on the closer side.

Subject to certain restrictions, some of which are mentioned in a preceding paragraph, it is possible that the closest workable setting on rovers using the same type of three-line system as the machine used in these experiments, would produce the strongest yarns.

The behaviour of the Light-middle-top-roller system on the 111g frame was complex, both front to middle and middle to back line settings exerting effects which were not always parallel to each other. A setting of 29-50 could be used as a provisional basis when in doubt for cottons within the range of the shorter and medium stapled Egyptian cottons, perhaps 31-50 would be a comparable basis for longer stapled samples.

Over the Egyptian range, in all but the most exceptional of circumstances, it appears likely that the closest settings of Casablanca systems give best results from the point of view of resulting yarn strength, and little, if any, changes appear to be required when a new cotton is introduced.

#### REFERENCES

- <sup>1</sup> Hancock, H. A. A Spinning Procedure for Cotton Samples. *J. Text. Inst.*, 1937, 28, T161.
- <sup>2</sup> Hancock, H. A., and Dunkerley, F. Relative Yarn Strengths using Casablanca and Three-line Draft Systems at the Speed Frames. *This Journal*, T193.

Received 11/7/41

## 14—RELATIVE YARN STRENGTHS USING CASABLANCAS AND THREE-LINE DRAFT SYSTEMS AT THE SPEED FRAMES

By H A HANCOCK and F DUNKERLEY

(Ministry of Agriculture, Egypt)

*Copyright by the Textile Institute*

### SUMMARY

Spinning-test results, using ordinary draft systems at the speed frames, with rollers reset for each cotton, are compared against tests using Casablancas apron system at the speed frames, working at a fixed setting for all Egyptian cottons. The ranking order of samples is found to be closely similar whichever draft system is used, to the advantage of the apron system because its testing technique is faster.

A small displacement of values is noticed with combed staples processed by the apron system, an effect ascribed chiefly to the higher regularity of combed cotton, but the effect is of negligible importance over the range of staple irregularity found in Egyptian raw cottons.

---

With spinning-tests on large numbers of cotton samples, such as are dealt with in plant selection work, an undesirably large part of the working time has to be spent with a roller-setting gauge at the speed frames. So as to reduce this time factor, it has been proposed<sup>1</sup> to eliminate roller setting operations at the speed frames by use of the Casablancas draft system working at low draft and at fixed setting for all Egyptian cottons. It was, of course, important to know if the new technique introduced characteristics of its own into the test results, and it was shown that the ranking order of 50 cottons uniformly processed in this way was similar to that of the same samples processed on conventional draft systems, with roller settings adjusted to each cotton individually.

The experiments on roller settings recorded in a recent paper<sup>2</sup> offer an opportunity of recomparing results from the two types of draft system, with the aim of confirming that the ranking order of yarn strengths is the same by either method of testing. These experiments on the 18 Egyptian cottons listed in Table I were more precise and covered a wider range of staple types than had been studied hitherto, the longest and shortest in the Egyptian range were represented, and the range of staple irregularity was extended to include low and high grade cottons, combed and double combed preparation. Roller settings for highest yarn strengths were determined at slubber, intermediate and rover for the three-line draft systems, working at the usual draft of five, and these strengths may be compared with those from the Casablancas system *working at the same draft* under identical conditions, except that the Casablancas roller settings were the same for every cotton. Comparison of the draft systems at the three speed frames alone is discussed here, all rovings having been treated identically at the ring frame and spun into 60's twist on a frame fitted with Casablancas draft system.

**Table I**  
**Description of Samples Tested**

	Hair Weight	Staple Length	LEA PRODUCT		Increase % of Casablanclas
			3-Line	Casablanclas	
Zagora FGF	176	40	1392	1490	7 0
Uppers FGF	172	40	1725	1798	4 1
Sakel FGF	130	43	2305	2397	4 0
Sakel FGF	128	42	2265	2380	5 0
Giza 26 FGF	112	51	2665	2792	5 0
Zagora FG	185	41	1640	1732	5 7
Giza 12 FG	147	44	2290	2382	4 0
Giza 7 FG	148	45	2510	2612	4 1
Domans Sakel Extra	123	51	3000	3172	5 8
50 50 mixing Uppers	—	51	2207	2305	4 5
FG and Sakha 4 FG					
Zagora FG Combed	186	41	1957	1982	1 3
Zagora FG Dble Combed	185	41	2035	2052	1 0
Uppers FG Combed	179	40	1962	2010	2 3
Giza 12 FG Dble Combed	142	48	2697	2755	2 1
Sakel FGF Combed	128	46	2732	2797	2 3
Sakha 4 FG Combed	122	50	3117	3212	3 0
Giza 26 FG Combed	128	49	3318	3402	2 9
Giza 26 FG Combed	123	53	3322	3340	0 5

## NOTES TO TABLE 1

The single combings were all 20% waste, the double combings 36% waste in two operations. Hairweights are in 00 mgrm units per cm. Staple length is measured by the "half-fall" of the Balls Sorter. Lea products in 60s ring twist are given for the three-line system working at optimum settings at slubbei, inter and rover for each cotton, and for the Casablanclas system at fixed settings for all the cottons.

These results are assembled in Fig. 1A as a correlation diagram of lea products, and it will be seen that the points fall along two lines, one for the combed cottons and another for the carded. Increased yarn strengths are obtained from Casablanclas prepared rovings both with combed and with uncombed cottons, but the increase is consistently greater with uncombed cottons and these points form the second line. When the Casablanclas results for combed cottons are increased by 3 per cent, all points are found to fall along a single line (Fig. 1B), and yarn strengths by the two methods of testing give a correlation coefficient of  $r=1.00$ .

Some selective action of the apron system in favour of less regular staples had been previously considered as a possibility,<sup>3</sup> as it might be argued that this system supports the floating fibres of more wasty cottons and therefore drafts them with higher efficiency than does the ordinary three-line system. Such selective action is apparently found, but it is sufficient to change relative values only when the range of staple irregularity is very great, as when combed and uncombed cottons are compared, and perhaps even then only when augmented by the effects of hair parallelism. A rough guide to comparative irregularity or wastiness is given by the percentage of staple less than  $\frac{7}{8}$  in in length, as determined by the Balls Sorter, with typical samples, this value is about 11 per cent for combed cotton, 23 per cent for uncombed high grade, 29 per cent for uncombed low grade cotton, so that

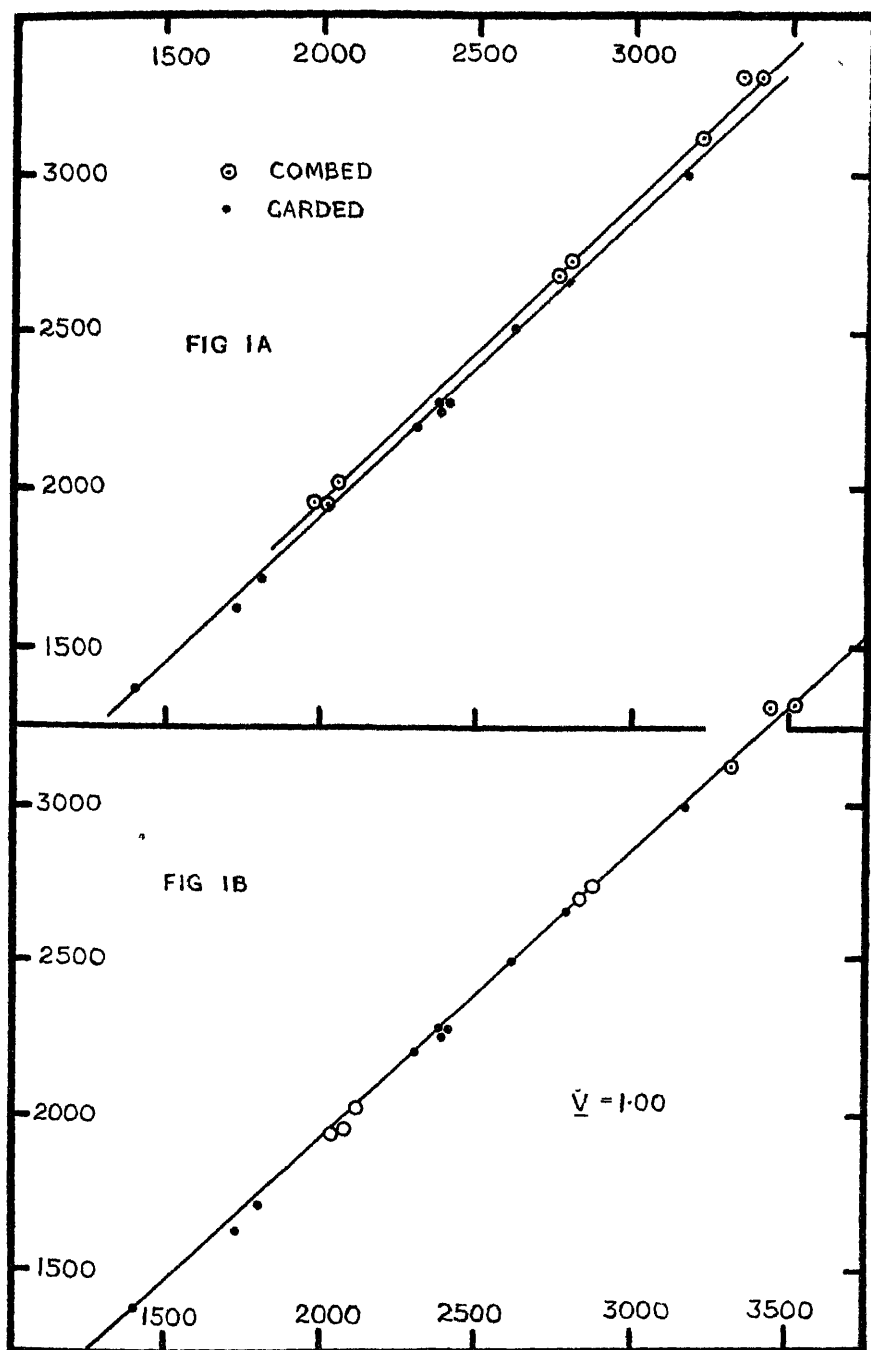


Fig 1 Lea Product Casablanca Processed Rovings  
Yarn strengths using different draft systems at the speed frames only  
In the lower diagram, the Casablanca processed combed yarns have their strengths increased by 3%, when they fall in line with the carded yarns.

combed cotton stands well away from either grade of uncombed as regards wastiness. This may be why no appreciable selective action can be distinguished between raw cottons, nor over the range of staple irregularity between Fully Good and Fully Good Fair cottons (Table II).

**Table II**  
**Increased Strength of Yarn from Casablancas Processed Rovings**

	8 Combed or Dble. Combed Cottons	5 High Grade (FG) Uncombed Cottons	5 Low Grade (FGF) Uncombed Cottons
Type of Staple Average Strength Increase	Very Regular 1.9%	Less Regular 4.8%	Least Regular 5.2%

The faster spinning-test technique using Casablancas draft system at the speed frames is thus shown to place cottons in closely similar ranking order to that given by conventional technique, but with a small error if relative strengths of combed and uncombed cottons are to be considered. In spinning-test work on growers' samples, the latter contingency does not normally arise, if it should arise when using the faster technique, a displacement of strength values in the combed samples has to be allowed for, and may be corrected by adding 3 per cent to these values.

#### REFERENCES

- <sup>1</sup> Hancock, H. A. A Spinning Procedure for Cotton Samples. *J. Text. Inst.*, 1937, **28**, T 161.
- <sup>2</sup> Dunkerley, F. Yarn Strength and Roller Settings. *This Journal*, 1179.
- <sup>3</sup> Dunkerley, F. Yarn Strength of Egyptian Mixings. *J. Text. Inst.*, 1937, **28**, T 255.

*Received 11/7/41*

## 15—YARN STRENGTHS OF EGYPTIAN MIXINGS. THREE-LINE ROLLER SYSTEMS.

By F. DUNKERLEY

(Ministry of Agriculture, Egypt)

*Copyright by the Textile Institute.*

### INTRODUCTION

During a recent series of experiments in drafting and roller setting, opportunity was taken to repeat the mixings experiments, using three-line systems at all stages, including the Ring Frame. At the same time, repeat experiments on the Casablancas were carried out alongside the Three-line tests to confirm previous results and to provide a comparative basis for consideration of the strength levels. It will be remembered that, in the original investigation, the yarn strengths of the mixings were roughly 2 per cent higher than would be expected from calculations based on the yarn strengths and proportions of the components.

### COTTONS USED

Two samples of cotton were bought in the market at Alexandria, exactly as similar samples of larger size would be bought by a mill in, say, Liverpool, or Manchester. They were not in any sense experimental growings and their exact origins were unknown. They were Sakelarides, grade Fully Good Fair, Uppers, also grade Fully Good Fair.

### EXPERIMENTAL PROCEDURE

The Standard Spinning Test Mill technique was employed, no opening machinery, double carding with the first card hand fed, three drawings (For details, see Hancock, *J. Text. Inst.*, Vol. 28, T161, 1937).

Mixings were made at second drawing stage in the following proportions:—  
(1) 100 per cent. Uppers, (2) 87.5 per cent Uppers, and 12.5 per cent Sakel, (3) 75 per cent and 25 per cent., (4) 50 per cent and 50 per cent., (5) 25 per cent and 75 per cent, (6), 100 per cent. Sakel.

The following table gives details —

Sample	Machine	Hank Delivered	WASTE PERCENTAGES			Wastes Both Cards
			Taker-in	Flats	Total	
Sakel FGF	First card	0 20	3 80	1 11	4 91	8.77
	Second card	0 26	2.23	1 63	3 86	
Uppers FGF	First card	0 20	6 00	0 65	6 65	11.40
	Second card	0 26	3.23	1.52	4 75	
	Draw frame	0 26 for both cottons at third draw 0 26 for the mixings at third draw				

The table below gives a list of roller sizes, etc —

Machine	Rollers	Back	Middle	Front	Break Draft	Total Draft	Hank	Spindle Speed
Slubber	Top	1 $\frac{1}{8}$ *	1 $\frac{1}{8}$ *	1 $\frac{1}{8}$ *	1 05	5	1 30	600
	Bottom	1 $\frac{1}{8}$	1 $\frac{1}{8}$	1 $\frac{1}{8}$				
Inter Rover	As for the Slubber above				1 05	5	3 25	600
	Top	2	1 $\frac{1}{8}$	1 $\frac{5}{8}$ *				
Ring	Bottom	1 $\frac{1}{2}$	1 $\frac{1}{2}$	1 $\frac{1}{2}$	1 17	15	60 00	8000
	Top	2	1 $\frac{1}{8}$	1 $\frac{1}{8}$ *				
	Bottom	1	1 $\frac{1}{8}$	1				

Weighting —All front rollers dead weighted

Middle and back on Slubber and Inter dead weighted by saddle

Middle and back on Rover and Ring self-weighted, steel, plain

\* Indicates cork covered rollers

It will be noticed that there was very little which was unusual in any of the systems, they were much as might be met with in an ordinary mill. The biggest problem in respect to the rollers of the Three-line systems would be normally that of correct roller settings, but for these experiments the problem of settings was simplified, because the two cottons used in these experiments had been previously employed in a series of roller settings experiments and the optimum settings for strength were known. These settings were therefore taken, the optimum for Sakel designated "Wide", the optimum for Uppers, "Close", a setting intermediate between these optima, "Normal". The intermediate setting was that thought appropriate for a 50.50 mixing, that is, half-way between the others. As "Close" and "Normal" gave nearly equal results, only "Close" and "Wide" are given in the following table.—

#### ROLLER SETTINGS.

Machine	Treatment	Settings in 1/32 inch units	
		Front-middle	Middle-back
Slubber	"Wide"	52	60
	"Close"	42	55
Inter Rover	Treatments and settings as Slubber		
	Treatments and settings as Slubber		
Ring	"Wide"	32	56
	"Close"	28	52

Whilst the foregoing experiments were being prepared, identical samples were processed and spun on Casablancas Apron systems at each stage under parallel conditions. The Casablancas systems on the speed frames were all set as closely as possible, these settings having previously given the highest strengths. For spinning, done at the same time as the Three-line spinnings, three settings were adopted, closest possible,  $\frac{1}{16}$  in. wider, and  $\frac{1}{8}$  in. wider.

#### DISCUSSION OF RESULTS

As a result of previous work, using Casablancas drafting systems throughout, certain conclusions were put forward. The conclusions were that the yarn strength of a 50.50 mixing of Egyptian cottons was near to the average yarn strength of the two components spun unmixed, that cottons contributed their undiminished quota to the yarn strength of a mixing, however many components there were and in whatever proportions they were mixed, that actual mixings tended, on the average, to be of slightly higher yarn strength than was to be expected from the strengths and proportions of the components.

The object of the present experiments was to find out if similar results would be obtained from three-line and light-middle-top-roller drafting systems. Figure 1 shows the yarn strengths of the samples according to the treatments adopted. Treatments effects on the yarn strengths were not

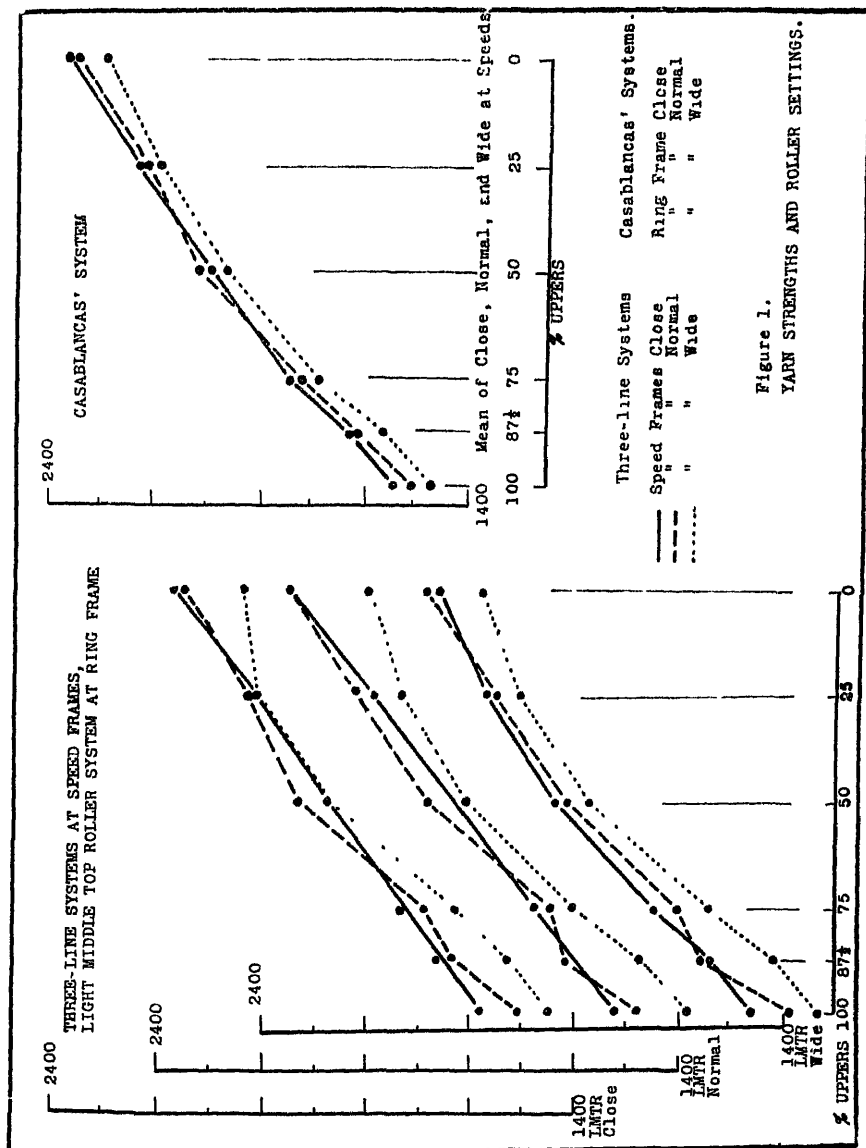


Fig. 1. Yarn Strengths and Roller Settings.

large within the range of settings adopted, though yarn strengths fell with wider settings. The closest settings were the closest possible on the machines as supplied by the makers.

Table I gives the relationship between the actual lea products of the mixings, from the closest settings of each roller system at each stage, and



those calculated from the strengths and proportions of the cottons mixed. The actual strength of a 50 : 50 mixing was near to the calculated strength, a result parallel to that found by Casablancas systems. When cottons were mixed in other proportions than 50 . 50's, the yarn strengths of the mixings were not diminished but were near to the strengths calculated from the strengths and proportions of the cottons mixed. Over the whole of the experiments carried out in this investigation, there was an average increased strength for the mixings of 2.6 per cent on the three-line and light-middle-top-roller systems, against 2.1 per cent. on the Casablancas systems working under comparable conditions. The conclusion drawn was that parallel results are produced by the three-line and light-middle-top-roller systems, working at optimum settings for each sample, and by Casablancas' systems working at identical settings for all samples, when the two systems are working at equal drafts and speeds.

TABLE I  
Mixings spun on Casablancas and on Ordinary Draft Systems

Lea products in 60's carded ring twist.

Per cent of Uppers . .	100	87.5	75	50	25	0
Per cent of Sakelarides	0	12.5	25	50	75	100
CASABLANCAS THROUGHOUT.						
(A) Actual lea product . .	1760	1831	1933	2101	2214	2412
(B) Lea product calculated by proportion . .		1842	1923	2086	2249	
Ratio A/B . . . . .		99.5	100.6	100.8	98.5	
THREE-LINE AT FRAMES :						
L M T R AT RINGS						
(C) Actual lea product . .	1583	1656	1737	1875	2016	2165
(D) Lea product calculated by proportion . .		1661	1729	1874	2019	
Ratio C/D . . . . .		99.6	100.7	100.0	99.8	
PERCENTAGE GAIN OF CASABLANCAS						
Ratio A/C . . . . .	111	111	111	112	110	112

NOTE—The comparison is between the yarn strengths from the "close" (i.e., closest possible with the given roller systems) settings of both systems at each stage.

#### REFERENCE

- <sup>1</sup> Dunkerley, F. Yarn Strength of Egyptian Mixings. *J. Text. Inst.*, 1937, 27, T 255.

Received 11/7/41.

# THE JOURNAL OF THE TEXTILE INSTITUTE

## TRANSACTIONS

### 17—MODIFIED STARCHES. Part IV. ACTION OF ALKALIS ON STARCHES

By G. B. JAMBUSERWALA

*Copyright by the Textile Institute*

Small quantities of alkalis added to starch pastes help to give them higher fluidity in a manner that acids, oxidising agents, enzymic materials, etc., affect starches. Brown and Heron<sup>1</sup> found that the viscosity of starch pastes is greatly affected by the treatment to which starch has been previously subjected, being greatly diminished if it has been treated with either acid or alkali. Reyche<sup>2</sup> has observed that starch is rapidly gelatinised at the ordinary temperature by sodium or potassium hydroxide but not by ammonia. Maquenne<sup>3</sup> has suggested that the coagulation of starch solutions on keeping is prevented by the presence of alkalis. Again, Samco<sup>4</sup> has indicated that starch is considerably modified by the prescribed treatment with alkalis. Alkalis convert starch into its soluble form, and the degree and rate of action depend upon the hydroxyl-ion concentration, the temperature and the period of the reaction, and the proportion of water to starch. When starch is made into a thin fluid mass with water, and alkali is slowly run into it with constant stirring, the starch granules swell and burst into a clear jelly. Such alkali treated starches have been long since employed as adhesives. In the present investigation, four varieties of starches were modified under prescribed conditions, using different alkalis of varying concentrations, and the properties of the products so obtained have been studied on the lines indicated in the previous publications of the author and his collaborator<sup>5</sup>.

The action of alkalis on starch is of considerable technical importance because it forms the basis of the manufacture of soluble starch and also of various processes for converting starch into products commonly known as vegetable gums. Most of these consist in treating starch with alkaline substances in one form or another. Gerard (Fr P 102,200, 1874) was the first to produce "Apparatine" by alkali treatment of starch. Marsden (U S P 376,445, 1888) patented an adhesive preparation in which starch was mixed with alkali and ammonium sulphate. Saare<sup>6</sup> discussed various starch glazing products prepared by the aid of alkalis. Kantorowicz (G P 157,896, 158,861, 1903) treated starch with alkali in alcoholic solution to give a product capable of gelatinising in the cold. A similar product was obtained by stirring starch in a concentrated solution of sodium sulphate and then introducing caustic soda solution (Fr P 365,834, 1906). Wulkan (G P 223,301, 1908) dried a mixture of starch and ammonia in thin layers by hot plates, which yielded a product with adhesive properties. The Arabol

Manufacturing Co (Fr P 397,167, 1908) produced a product capable of swelling in cold water by treating starch with a thiocyanate. In 1912, Perkin (U S P 1,020,655) treated starch with enough alkali to make a fluid adhesive that could be used in place of animal glues. F Sichel Kommandit-Ges and E Stern (G P 389,748, 1920) mixed starch with a little sodium aluminate or silicate, dried the paste at a high temperature quickly, and obtained a modified product. Singer (E P 188,344, 1922) obtained a product capable of swelling in cold water by simultaneous dry-grinding of raw starch and intimately mixing with dry caustic soda. Runge (G P 381,586, 1922) obtained a product readily forming paste with cold water by stirring starch with a saturated solution of an alkaline earth hydroxide at 70°-80° C. Supf obtained a similar product by treatment with concentrated caustic alkali hydroxide below 0° C (G P 351,370). Borax (Fr 806,678), water soluble phosphorus compounds (G P 644,027), and alkali thiocyanates (B P 464,606) have also been employed by various patentees to modify starch.

The extent of modification of modified celluloses is measured by the viscosity of their solutions in cuprammonium<sup>7</sup>, and similarly viscometric methods have, in fact, been used for the characterisation of modified starches. The chief difficulty in applying such methods to starch is that no entirely satisfactory solvent is available. The less modified starches always swell before dissolving and the swollen granules can be dispersed only by heating to a high temperature, which tends to cause further modification. Commercial starches are sometimes graded by the fluidity of their solutions in 1 per cent sodium hydroxide<sup>8</sup>, but these solutions change in viscosity with time and are also sensitive to mechanical treatment and to impurities. The most satisfactory solvent for starch yet found for use in viscosity measurements is an aqueous solution containing 30 g of calcium thiocyanate in 100 c c. Richardson<sup>9</sup> measured the relative viscosity of 1 per cent starch in this solvent by means of a capillary U-tube.

#### EXPERIMENTAL

##### Modification of Starches.

Samples of 100 g each of dried corn, sago, wheat and farina starches were treated separately with 200 ml of sodium hydroxide, potassium hydroxide, trisodium phosphate and sodium carbonate solutions of the undermentioned concentrations, calculated on the weight of starch

	Sodium hydroxide	Potassium hydroxide, Trisodium phosphate and Sodium carbonate
Corn, sago and wheat starches	1%, 2.5%, 4%	2%, 6%, 10%
Farina starch	1%, 2%, 2.5%	2%, 4%, 6%

These alkaline solutions were added to the flask containing the weighed starch gradually with vigorous shaking and without allowing either the temperature (30° C) to rise or the treated mass to turn into a jelly. The treatment was confined to 20 hours, the product was neutralised with dilute acetic acid, and finally the mass was washed free from alkali or acid by centrifuging, and dried first on porous tiles and then at 105° C. It may be noted that though initially no difference in the appearance of starch was observed on addition of sodium and potassium hydroxides of concentrations just over those mentioned above, the treated mass soon became nearly translucent. Therefore care was taken to employ such concentrations of

alkalis for each individual variety that the starch did not turn into a transparent gummy mass. Under the microscope these products did not appear to have their granules broken up except those produced by the higher concentrations of sodium and potassium hydroxides, where some of the granules appeared to have been burst by the alkaline treatments.

#### Alkali-labile Values.

Since the present products are but slightly degraded, their reducing values were not determined. The alkali-labile values were estimated on the lines indicated in the previous publications (*loc. cit.*), and the results are set out in Table I, column 6.

#### Viscosity Measurements.

These measurements were made as described in the previous publications by means of a Hoppler viscosimeter using 1 per cent. starch paste at 30°C., and the results converted into centipoises are set out in column 3. These, in turn, were converted into  $\log \eta$  (column 4) because these values present greater differences between the differently graded modifications of starches and at the same time help to give more readable graphs.

#### Thiocyanate Viscosity Determinations.

To 25 ml. of starch paste of 4 per cent. concentration, strong calcium thiocyanate solution (about 50 per cent.) was added such that, when made up to 100 ml. by dilution with water, the solution contained 30 g. of calcium thiocyanate plus 1 g. of starch in the 100 ml. of solution. This was kept for 30 minutes. Another calcium thiocyanate solution containing 30 g. in 100 ml. was prepared to serve as a standard. The times of falls of a ball in these two solutions were noted in a Hoppler viscosimeter, and the "thiocyanate viscosity" (column 5) was deduced from the following relation, as suggested by Richardson<sup>9</sup>.—

$$TV = \frac{1}{c} \cdot \log \frac{a}{b}$$

where  $a$  stands for the time of fall of the ball in calcium thiocyanate solution containing 30 g. of thiocyanate plus 1 g. of starch in 100 ml. of the solution,

$b$  stands for the time of fall of the ball in the standard 30 per cent. calcium thiocyanate solution,

and  $c$  is the concentration of starch in the thiocyanate solution.

#### Ash Content Determination

Properly dried starch was accurately weighed out (about 4 g.) in a silica crucible and incinerated in a muffle furnace at about 900° C. for six hours and weighed to a constant weight (column 7). The results indicate that no free alkali is left in the starches after the alkaline treatments.

#### CONCLUSIONS.

1 Alkalis modify starches in accordance with their hydroxyl ion concentration, and it is observed in Figs. 1 and 2, that caustic soda is the most effective, followed by caustic potash, trisodium phosphate and sodium carbonate in the decreasing order of effectiveness.

Table I

(1)	(2)	(3)	(4)	(5)	(6)	(7)
Starch	Percentage of the alkali concentrations on the weight of starch	Aqueous viscosity of 1% starch paste at 30° C in centipoises	Log of aqueous viscosity of 1% starch paste at 30° C in centipoises	Thiocyanate viscosity $T V = \frac{1}{c} \log \frac{a}{b}$	Alkali-labile values in mg of iodine for 100 mg of starch	Percentage of ash content
Farrow	—	3 329	0 5223	0 5500	26.2	0.37
	1% NaOH	3 052	0 4846	0 5291	26 84	0.198
	2% NaOH	2 441	0 3876	0 4199	27 35	0.9595
	2.5% NaOH	2 214	0 3452	0 4138	27 60	0 95
	2% KOH	2 500	0 3979	0 5032	26 25	0 2297
	4% KOH	2 135	0.3295	0 4279	27 27	0 995
	6% KOH	2 081	0 3138	0 3284	27 90	0 95
	2% Na <sub>2</sub> CO <sub>3</sub>	3 188	0 5035	0 5489	26 0	0.218
	4% Na <sub>2</sub> CO <sub>3</sub>	3.101	0 4915	0 5418	26 25	0 231
	6% Na <sub>2</sub> CO <sub>3</sub>	2 874	0 4585	0 5325	26 52	0.1728
	2% Na <sub>3</sub> PO <sub>4</sub>	3 118	0 4939	0 5441	25 73	0 2018
	4% Na <sub>3</sub> PO <sub>4</sub>	2 918	0 4641	0 5395	25 95	0 227
	6% Na <sub>3</sub> PO <sub>4</sub>	2 718	0.4343	0 5277	26.4	0.188
Corn	—	1.684	0 2264	0 4990	16.60	—
	1% NaOH	1 545	0.1889	0.3767	17.90	0.1288
	2.5% NaOH	1 516	0 1807	0 3450	19 39	0 638
	4% NaOH	1 445	0 1599	0.2663	22 27	0 806
	2% KOH	1 516	0.1807	0 3361	17 55	0 116
	6% KOH	1.463	0 1653	0 3311	18 49	0.2253
	10% KOH	1 358	0 1329	0.2676	22 04	0 2574
	2% Na <sub>2</sub> CO <sub>3</sub>	1 554	0.1914	0.4056	17 2	0.2659
	6% Na <sub>2</sub> CO <sub>3</sub>	1 544	0 1886	0 3942	18 05	0 2813
	10% Na <sub>2</sub> CO <sub>3</sub>	1 516	0.1807	0 3468	18.95	0 2321
	2% Na <sub>3</sub> PO <sub>4</sub>	1.556	0.1920	0.3789	17 49	0 5697
	6% Na <sub>3</sub> PO <sub>4</sub>	1.516	0 1807	0.3639	18 30	0 1826
	10% Na <sub>3</sub> PO <sub>4</sub>	1 439	0 1577	0 3358	19.20	0 3539
	—	1 820	0.2622	0 4279	15 91	0 27
Sago	1% NaOH	1 776	0.2495	0 4260	17 03	0 0632
	2.5% NaOH	1 723	0 2363	0 3979	18 24	0 162
	4% NaOH	1.623	0.2075	0.2849	19 41	—
	2% KOH	1 751	0.2432	0 4162	17 73	0 102
	6% KOH	1 723	0 2362	0 3947	18 80	0 135
	10% KOH	1 516	0 1807	0 2829	20 25	—
	2% Na <sub>2</sub> CO <sub>3</sub>	1 776	0 2495	0 4218	17 12	0 1496
	6% Na <sub>2</sub> CO <sub>3</sub>	1 776	0 2495	0.4199	18 25	0 1888
	10% Na <sub>2</sub> CO <sub>3</sub>	1 731	0 2382	0 3900	19 45	0 1972
	2% Na <sub>3</sub> PO <sub>4</sub>	1.776	0 2495	0 4199	17 3	0 1681
	6% Na <sub>3</sub> PO <sub>4</sub>	1 751	0 2432	0 4012	18 5	0 1992
	10% Na <sub>3</sub> PO <sub>4</sub>	1 693	0 2287	0 3691	19 5	0 1597
	—	1 407	0 1480	0 2822	22 44	0 4
	1% NaOH	1 357	0 1316	0 2617	22 9	0.132
Wheat	2.5% NaOH	1 307	0 1161	0 2344	23 8	0 176
	4% NaOH	1 255	0 0984	0 2127	24 24	0 4035
	2% KOH	1 307	0 1161	0 2499	23 22	0 1458
	6% KOH	1 280	0 1073	0 2314	24 4	—
	10% KOH	1 229	0 0893	0 2219	25 25	—
	2% Na <sub>2</sub> CO <sub>3</sub>	1 357	0 1316	0 2818	22 8	0 2129
	6% Na <sub>2</sub> CO <sub>3</sub>	1 357	0 1316	0 2789	23 48	0 1548
	10% Na <sub>2</sub> CO <sub>3</sub>	1 322	0.1236	0 2694	23 61	0 0939
	2% Na <sub>3</sub> PO <sub>4</sub>	1 357	0 1357	0 2720	22 49	0 1764
	6% Na <sub>3</sub> PO <sub>4</sub>	1 322	0 1236	0 2617	23 29	0 1818
	10% Na <sub>3</sub> PO <sub>4</sub>	1 307	0 1161	0 2558	24 22	0 284

2. Wheat starch is least affected by the alkali treatments followed by corn, sago and farina starches in the increasing order. This order is slightly different from the one found for modified products obtained by treatments with acids, oxidising agents, etc., where corn starch precedes wheat, followed by sago and farina starches, as indicated in the previous publications.

3. Though Fig. 1 indicates that alkali-labile values for wheat starch modifications are greater than those for corn and sago starches, it may be pointed out that raw wheat starch has a greater alkali-labile value than the other two untreated starches, and the increase in alkali-labile values on alkali treatments is greater in the last two starches as compared with that in wheat starch.

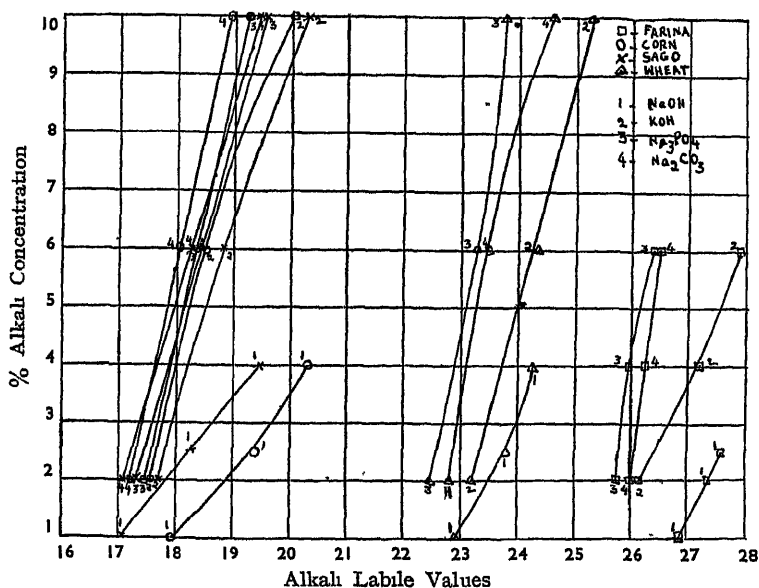


Fig 1.

4 The relation between alkali concentrations and viscosities of starch pastes is almost linear, a sharper fall in viscosity is observed with caustic soda modifications (Figs. 3, 4, 5 and 6).

5. Thiocyanate viscosity has been found to be a more reliable measure for the extent of degradation effected in starches and the results could be reproduced with greater ease and precision as compared with viscosity measurements in aqueous solutions, because the method of preparing starch pastes influences considerably the viscosity results

6 These modified products obtained by alkali treatments not only possess the good points ordinarily found in thin boiling starches, but are free from the reducing and carboxyl groups that are usually found in products obtained by acid or oxidising agents and may therefore be preferred to the degraded products produced by other methods.

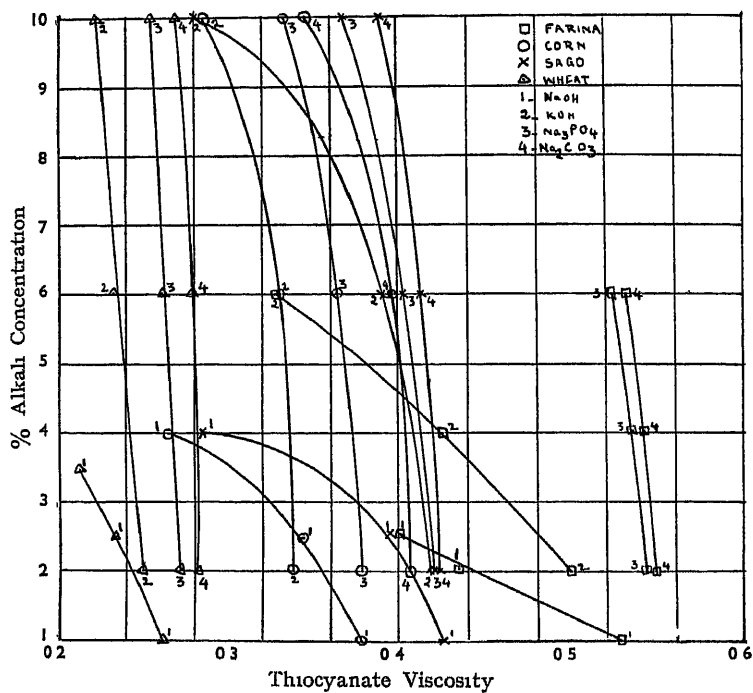


Fig. 2.

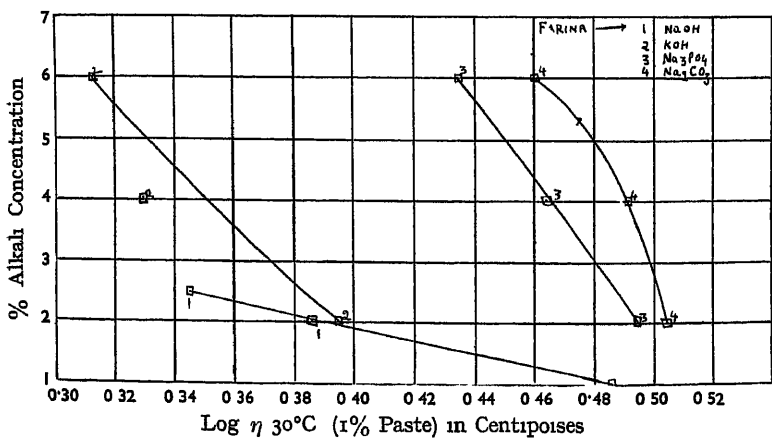
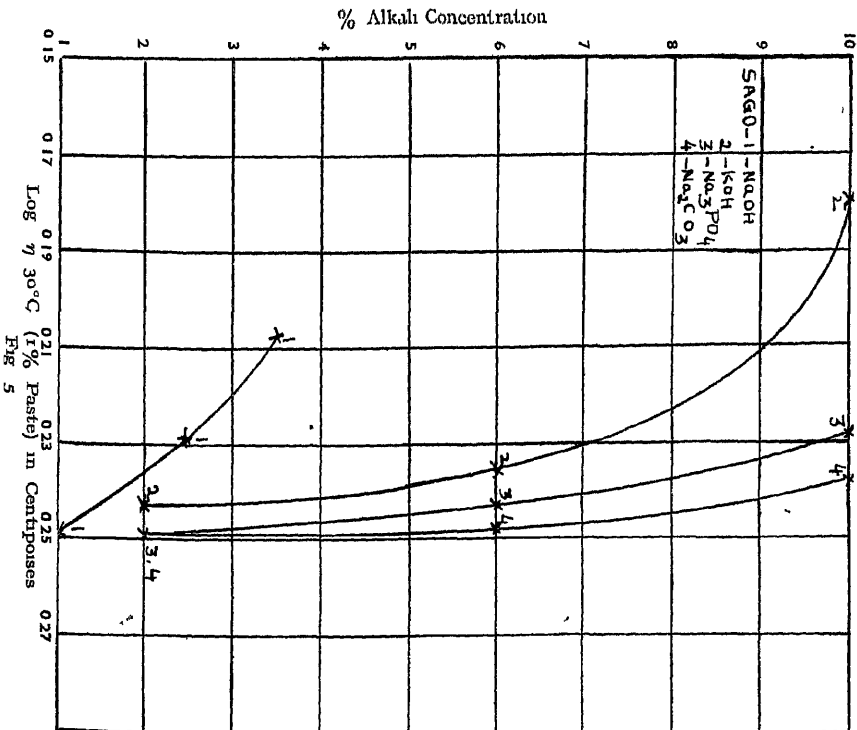
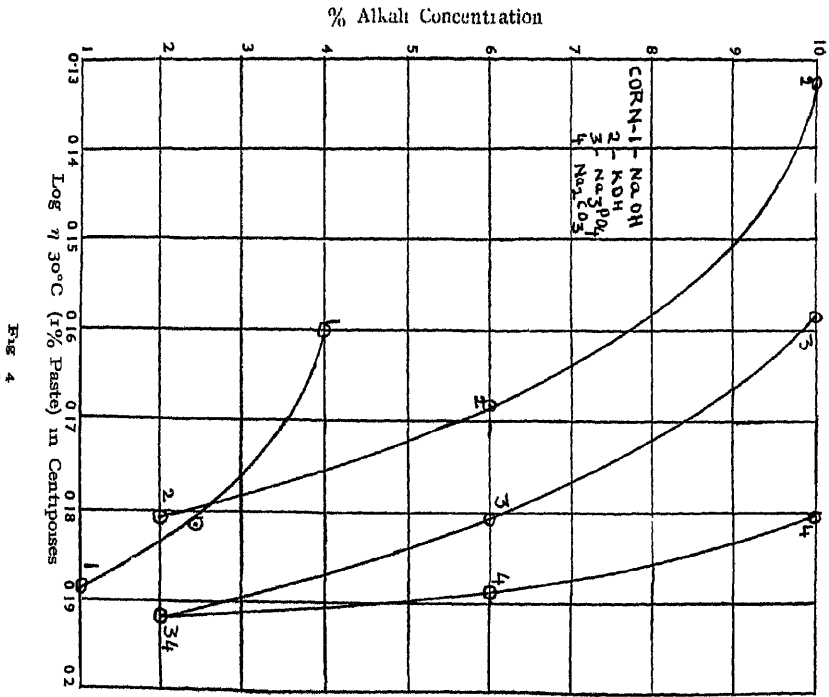


Fig. 3





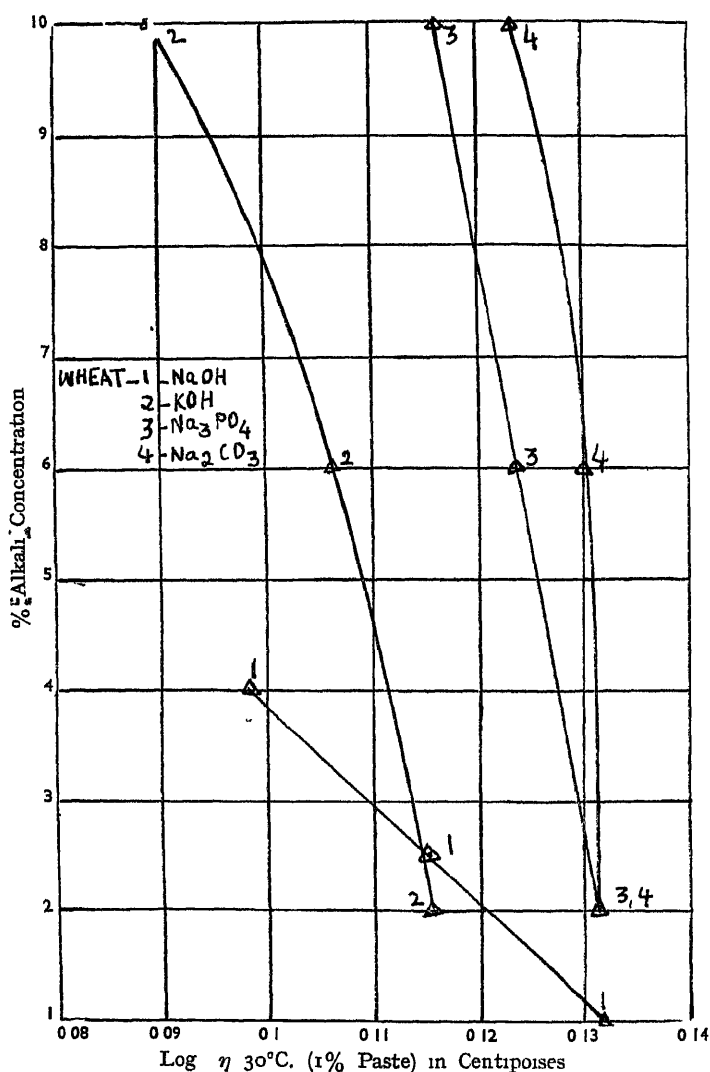


Fig 6

The author's thanks are due to Mr P Y Kulkarni, who carried out the experimental work

#### REFERENCES

- <sup>1</sup> Brown and Heon *J Chem Soc Trans*, 1879, 35, 614
- <sup>2</sup> Reyckler *Bull Soc Chim Belg*, 1920, 29, 118.
- <sup>3</sup> Maquenne. *C r Acad Sci*, 1903, 137, 1266
- <sup>4</sup> Samec *Biochemische Zeit*, 1921, 113, 255
- <sup>5</sup> Jambuserwala *J. Text Inst*, 1938, 29, T149, 1939, 30, T85; 1940, 31, T1
- <sup>6</sup> Saare. *Z Spiritusind*, 1901, 24, [44], 451 (Abstract in *J. Soc Chem Ind*, 1901, 20, 1206)
- <sup>7</sup> Clibbens and Geake *J Text Inst*, 1928, 19, T77.
- <sup>8</sup> Gallay and Bell *Canadian J Res*, 1936, 14B, 360
- <sup>9</sup> Richardson. *Chem and Ind*, 1939, 58, 464

# THE JOURNAL OF THE TEXTILE INSTITUTE

## TRANSACTIONS

### 18—STATISTICAL METHODS IN TEXTILE RESEARCH PART 4. THE DESIGN OF WEAVING EXPERIMENTS

By V. R. MAIN and L. H. C. TIPPETT

(British Cotton Industry Research Association)

*Copyright by the Textile Institute*

#### INTRODUCTION AND SUMMARY

For many years, experiments have been conducted at the Shirley Institute to measure the effects on warp breaks in weaving of conditions of the yarn preparation and loom settings, and attention has been paid in designing the experimental lay-out to reducing errors as far as possible and to measuring them, so that the statistical significance of the results could be tested. From the results of many experiments it is now possible to give a general account of the importance of the errors arising from various sources and to discuss the most economical arrangement for various types of experiment. Such is the purpose of this paper. The designs and methods used are similar to those originally developed for and largely used in agricultural field trials, and the terminology is that generally used in statistical writings on the subject.

Most of the experiments have been of the same kind, and have involved measuring differences in breakage rates between warps, which, during the course of the experiment, are interchanged between looms to give a Latin square design. A typical experiment is first described and analysed in detail to show the various sources of error and introduce the variances that measure their effects. Then, in the next section of the paper, the results of similar analyses for many experiments are summarised.

It is shown that there are differences between looms, and the various healds and reeds associated with them, in their tendency to cause warp breaks, the effects of these differences can be eliminated by a suitable experimental design. The remaining errors are random in that they cannot be associated with any controllable factors. Their expected variance is proportional to the mean warp breakage rate for all warps in the experiment, and is substantially greater than the value (calculated from the Poisson distribution) that would result if all the conditions were under perfect experimental control. An empirical formula is given for calculating this variance in terms of the mean warp breakage rate, the length of each "piece" of cloth and the number of pieces per warp.

In the final section of the paper, the general question of the design of weaving experiments is discussed in the light of the results of the previous section. The conclusion is reached that a randomised block design to eliminate loom and associated variations is better than the Latin square design, and that for some kinds of experiments a "split-plot" design can be adopted with advantage.

The error variance is a composite quantity made up of the effects of variations within pieces to which are added the effects of variations between pieces, and because of this there is an optimum piece-length which gives maximum precision for minimum cost. This length is worked out to be of the order of 60 yards.

There follows a discussion of the use of a transformation of the breakage rate results to make the error variance independent of the mean, and it is suggested that, owing to difficulties in the interpretation of results expressed in terms of the transformed variable, it is advisable not to use such a transformation. This involves avoiding complex experimental designs.

Finally, it is shown how interactions between various factors affect the generality of the results of an experiment, and how account should be taken of this in deciding the scale of replication. The main conclusion is that all experiments should be replicated as many times as possible, and that ideally the replicate warps should be sized on different occasions, with different deliveries of yarn and different values of all other "subsidiary" factors that vary in the field to which the results will be applied. Practical considerations, however, limit the application of this ideal principle.

#### A TYPICAL EXPERIMENT

Most experiments at the Shirley Institute have been concerned with measuring the effect on warp breaks in weaving of various amounts and kinds of size put on the warp, and in any one trial this has been done by preparing warps, each with a different sizing treatment, weaving the warps together in a group of looms, and counting the warp breaks. The immediate problem has been, therefore, to determine as accurately as possible, and measure the error in, the comparative mean breakage rates for the warps. It is customary and convenient in the experimental workrooms for one weaver to look after four looms, four sizing treatments are often a suitable number, involving four warps; and enough yarn is usually put on each beam for four pieces of cloth to be woven during four consecutive periods. This system lends itself to the Latin square arrangement, in which the warps are interchanged between the looms at the end of each period so that ultimately each warp has had one piece woven in each loom. One such arrangement woven in looms (1), (3), (4) and (7) is shown in Table I. The first piece of warp 426 is woven in loom (1), the second in loom (4), and so on. The warp breakage rates are also given. Now it can easily be seen that when all the results for each warp are averaged, the differences between the mean breaks for the four warps are not affected by such differences between the looms as are constant for all warps and periods, nor by the effects of such changes in weaving conditions (e.g. humidity of the atmosphere) from one period to another as influence all warps equally. In short, consistent loom and period effects are eliminated from the comparisons between warps.

Table I  
Latin Square Arrangement in Looms (1), (3), (4) and (7), and Warp Breaks per 10,000 Picks

Warp No —		426	427	428	429
Period	1	5 52 (1)	2 87 (4)	9 76 (7)	6 69 (3)
"	2	6 02 (4)	6 25 (7)	5 14 (3)	9 16 (1)
"	3	8 90 (7)	2 91 (3)	5 77 (1)	6 53 (4)
"	4	6 09 (3)	5 07 (1)	2 83 (4)	9 77 (7)

The results are treated by the analysis of variance<sup>1</sup> to show the magnitude of the warp, period and loom differences compared with the residual uneliminated error. The analysis for the data of Table I is in Table II. The warp variance is significantly greater than the residual, showing that the differences between warps are greater than can reasonably be attributed to uneliminated errors. The period variance is not greater than the residual, indeed it is less, but the difference is below the 5 per cent. level of significance. The loom variance is greater than the residual and is between the 5 and 1 per cent levels of significance, showing that there has been a gain in precision due to the adoption of an arrangement that eliminates the effects of loom differences. Had the arrangement been purely random, the residual variance would have been increased to 4.057, and the warp variance would have been something like  $(9.833 - 1.386 + 4.057) = 12.504$ , with a significance for 3 and 12 degrees of freedom that is just below the 5 per cent. level.

**Table II**  
**Analysis of Variance of Warp Breaks per 10,000 picks**

Source of variation	Sum of squares	Degrees of freedom	Variance
Warps ... ..	29.4984	3	9.833
Periods . . . .	1.1726	3	0.391
Looms . . . . .	39.1986	3	13.066
Residual (error) ..	8.3138	6	1.386
	} 48.6850		
		} 12	} 4.057
TOTAL ..	78.1834	15	—

A warp break is a chance event, and if the yarn quality and weaving conditions were uniform the residual errors would be expected to have the variance calculated from the Poisson distribution<sup>2</sup>. In this instance the mean breakage rate is 6.20, there are 28.81 units of 10,000 picks in each piece so that the expected residual variance assuming the Poisson distribution is  $6.20 \times 28.81 = 0.215$ . The actual variance of 1.386 is greater than this, showing that uncontrolled variations in conditions have, in this instance, increased the errors of the experiment.

The full data collected during the experiment permit another estimate of variance to be made. Each piece of cloth is sub-divided into a number of shorter lengths called "marks"; there may be as few as two or as many as ten marks per piece. The warp breaks in each mark are recorded separately and hence the variance between marks within a piece may be estimated and expressed as a ratio of the expected variance calculated from the mean breaks for the piece, assuming the Poisson law. Ratios for the separate pieces may be averaged for all pieces in an experiment. For the experiment under consideration there were 10 marks per piece and this ratio for the 16 pieces varied between 0.36 and 3.36 with an average of 1.16. If the yarn quality and weaving conditions were uniform for each piece, the variance between marks would, on the average, be that calculated from the Poisson distribution and the above ratio would be distributed as  $\frac{\chi^2}{9}$  for 9 degrees of freedom, with an average value of unity. The actual average is not far from unity.

### RESULTS OF MANY EXPERIMENTS

The following results do not all refer to exactly the same experiments. In some instances the data for the separate marks are not available and the corresponding ratios of variance are missing; and some experiments have been arranged as  $5 \times 4$  incomplete Latin squares and the analyses of variance between pieces for these have not been used, although they have provided data of the variance between marks within a piece.

There is a good deal of variation in results from one experiment to another, and any summary which is to be used as a basis for the design of future experiments must include the variable results. But a small number of experiments yield results that differ excessively from the remainder, and it is better to regard these as exceptional and to design future experiments on what may be regarded as the more normal experience than to include everything in the general summary. Any exceptional results that are obtained in the future may then involve special measures being taken, such as further repetitions of the experiment. Where something has obviously gone wrong with an experiment or part of it, and evidence of this is available other than the results, these results have been omitted from the following summary without doubt or difficulty. It is not so easy, however, where the only suggestion of abnormality lies in the data themselves. The authors have used their judgment and discarded results that were very different from the remainder, but have done this with restraint and only when the abnormality was so striking as to be obvious. Mention is made below where any data are so discarded.

#### Within-piece Variance

Values of the mean ratio of the variance between marks within a piece to the Poisson expectation are available for 40 experiments. The degrees of freedom on which these mean ratios were estimated vary between 16 and 160, most being about 30, and the values of the ratio range between 0.7 and 3.0 with an unweighted grand mean of 1.645. The mean ratios for the separate experiments show no signs of being correlated with the corresponding mean breakage rates, suggesting that the mean ratio is characteristic of the variance between marks within pieces for a given experiment, and that the grand mean ratio is a suitable summary of this variance for all experiments. In arriving at these results, about 3 per cent. of the individual ratios have been omitted because they differ extremely from the remainder.

#### Residual Variance between Pieces

The residual variance between pieces (i.e. the error variance obtained after eliminating consistent differences between looms, warps and periods), has been estimated from the analysis of fifty  $4 \times 4$  Latin squares. It varies considerably from one experiment to another but is usually very much greater than the expected variance calculated from the Poisson formula or the value calculated from the variance between marks within a piece. It is in accordance with statistical practice to regard each actual value of the variance as an estimate of a "true" variance that would have been obtained had the experiment been done with an infinite number of pieces. The estimates of variance, being based on only 6 degrees of freedom, differ considerably from the true values in a way that is random and follows known probability laws. An attempt will be made to obtain a general expression for the true variance.

The true residual variance between pieces may be regarded as made up of two parts, one due to the effect of the within-piece variation and the

other due to changes in weaving conditions and in yarn quality, including uncontrolled variations in sizing, from one piece to another. When the total variance is plotted against the mean breakage rate for all warps in each experiment, there is evidence of a positive correlation, the points being scattered about a line that could reasonably be drawn through the origin. Since the within-piece variance is usually a small part of the total, this result suggests that the added variance is proportional to the mean breakage rate, and that the true variance may be expressed by the following formula:

$$V = cB + \frac{kB}{N} \dots \dots \dots (1)$$

where  $V$  is the true residual variance,  $c$  is a constant,  $B$  is the mean breakage rate for all warps in the experiment,  $k$  is the ratio of the actual to the

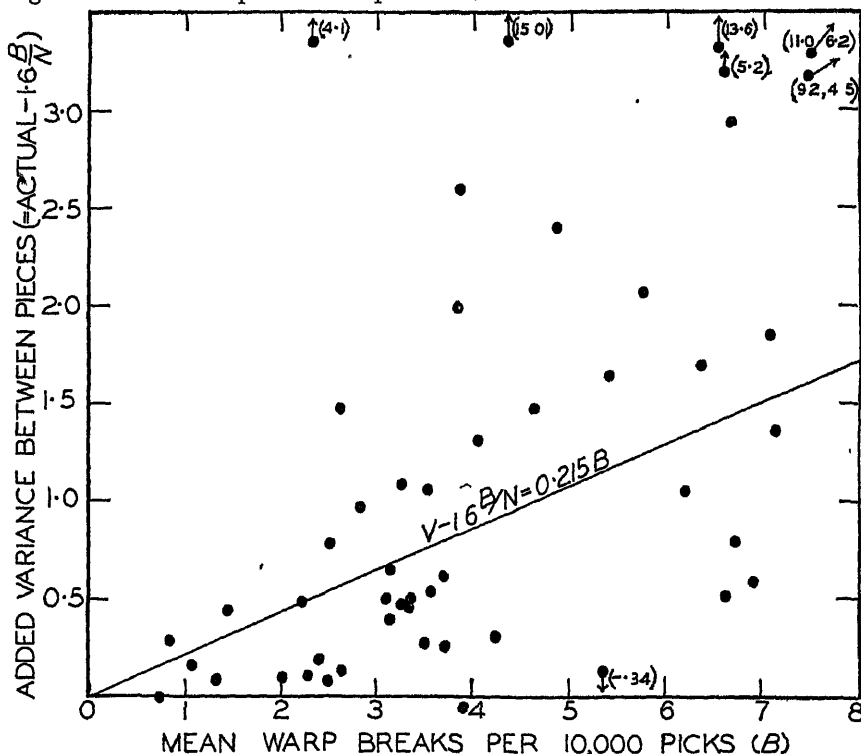


Fig. 1

expected variance between marks within a piece, and is at first taken to be 1.6, and  $N$  is the number of 10,000 pick units per piece of cloth.

The quantity  $B/N$  is the expected variance between pieces calculated from the Poisson distribution,  $kB/N$  is the variance between pieces due to the variance between marks within a piece and  $cB$  is the added variance between pieces due to changes in yarn quality and weaving conditions from piece to piece. To show how far equation (1) represents the data, the quantity (actual variance— $1.6B/N$ ) is plotted against mean breakage rate for the 50 experiments in Fig. 1. The points are all scattered about the straight line drawn through the origin, except perhaps for the 6 points at the top of the diagram that are "off the map". The degree of scatter increases as the mean breakage rate increases. This line may be taken as representing the true added variance, and its slope has been obtained by the method of least

squares, giving each point a weight inversely proportional to  $B$ , use has been made of the formula:  $c = \frac{S(v - 1.6B/N)}{SB}$

where  $S$  is the summation over all experiments, and  $v$  is the actual or estimated variance (as opposed to the true value denoted by  $V$ ). The six values shown at the top of Fig 1 were omitted and the remainder gave an estimate for  $c$  of 0.215. As an approximate simplified formula for calculating the true residual variance, the following is proposed:

$$V = \frac{1}{5}B + \frac{3}{2} \cdot \frac{B}{N} \quad \dots \dots \dots (2)*$$

If equation (2) fairly represents the true variance, the actual variance will only differ from the values calculated from (2) by the random errors inevitable in estimating variance from 6 degrees of freedom, and the ratios  $v/V$  will be distributed as  $\frac{\chi^2}{6}$  for 6 degrees of freedom. Table III compares the two distributions for the 44 experiments, omitting values corresponding to the points at the top of Fig 1 and the agreement is seen to be good. The ratios  $v/V$  for the 6 experiments omitted are respectively 1.2, 2.1, 2.2, 2.4, 5.9 and 13.2. The first four of these are within the limits of what might be expected from random fluctuations, but the ratios of 5.9 and 13.2 are altogether too high to be attributable to random fluctuations and indicate the operation of some exceptional cause of variation. On the whole, however, equation (2) provides a reasonably accurate estimate of what the true residual variance is likely to be.

**Table III**  
**Comparison of Distribution of  $\frac{\chi^2}{6}$  and Ratio  $\frac{\text{Actual}}{\text{Calculated}}$  Variance ( $v/V$ )**

$v/V$	Theoretical frequency of $\frac{\chi^2}{6}$	Actual frequency of $v/V$
0—0.5	8.4	6
0.5—1.0	17.0	19
1.0—1.5	11.0	12
1.5—2.0	4.9	3
2.0—2.5	1.8	3
Over 2.5	0.9	1
TOTAL	44.0	44

#### Warp Variance

The warp variance is not a characteristic of the method or design of the experiments but depends on experimental variations that are made arbitrarily, and therefore is of no importance in the present study.

#### Period Variance

The ratio of the period variance to the residual is above the 5 per cent level of significance on three occasions out of 50 and on no occasion is it above the 1 per cent. level. The ratio corresponding to the mean value of Fisher's  $z$   $\{ = \frac{1}{2} \log_e (\text{ratio of variances}) \}$  is 1.108. Thus, there are no appreciable variations from period to period, that affect all warps and looms equally and add to the residual variance.

\* A referee has suggested that the value of  $c$ , though calculated from 50 points, has still a certain standard error which he has worked out roughly at about 10%, taking  $N=16$ , and that it might be better to use, say, the upper 5% fiducial limit of  $c$ , to be on the safe side. This would mean writing  $\frac{1}{2}B$  for  $\frac{1}{5}B$  in equation (2). This modified value of  $c$  would not be the correct one to use in calculating Table III but its use might be advisable in further practical applications. The effect of such a change on the conclusions drawn in this paper would be negligible.

**Loom Variance**

The ratio of the loom variance to the residual exceeds the 5 per cent. level of significance in six experiments out of 50 and exceeds the 1 per cent. level in two. The ratio corresponding to the mean of values of Fisher's  $z$  is 1.38. Thus, there is a small but appreciable loom effect.

**DESIGN OF EXPERIMENTS****Loom and Period Effects and their Influence on the Design**

In any one experiment, the looms were usually of the same pattern, make and age, and were adjusted as similarly as possible. In interchanging warps between looms, the healds and reed remained in each loom throughout the experiment, the warp being cut out between the back-rest and beam at the interchange and the new one being twisted or knotted on to the ends remaining in the healds. Consequently, the so-called loom variance includes and may be largely comprised of the effect of differences between sets of healds and reeds. These differences have been kept to a minimum by using in one experiment sets of healds of the same age and state of wear. Although small, this effect is worth eliminating.

The absence of a period effect is perhaps to be expected, since the chief factors that could vary from time to time and have important effects on warp breaks, viz., the humidity and warp tension, are in the Institute's weaving shed controlled. In view of this result, there is no gain in accuracy by using the Latin square arrangement as opposed to a "randomised block" arrangement, in which each warp is woven equally in each loom but otherwise at random. In practice, however, since only one piece can be woven from a warp at one time, and it is convenient to weave four warps together, an experiment with four warps and four pieces per warp will almost inevitably be in a Latin square. An advantage of the use of the randomised block arrangement is that it is easy to compare more than four warps, and another is that the degrees of freedom on which the residual variance is estimated are increased, e.g. from six to nine for a  $4 \times 4$  experiment.

The residual variance, described by equation (2), is very much larger than the expected value that would be obtained if the control of yarn quality and weaving conditions were perfect. Usually  $N$  is at least 16, with a corresponding value of  $V$  of  $(\frac{1}{8} + \frac{8}{32})B$  or about  $3B/10$ , whereas the expected variance is  $B/16$ ; i.e. the actual residual variance is of the order of five times the expected. Of this variance, the variations from piece to piece account for about two-thirds ( $B/5$ ), and the variations within a piece for about one-third ( $3B/32$ ). The causes of these variations are not completely known, but it is probable that the between-piece variations are largely due to changes in the general gaiting of the looms occurring at the interchanges. This occurs in spite of attempts to standardise as far as possible the gaiting technique and loom settings. However, although this process of interchanging increases the apparent errors of the experiment, it must be done. Each warp must necessarily be gaited in the loom independently and warp differences are affected by gaiting variations, consequently, if these were not also included in the estimate of error there would be a danger of attributing false significance to apparent warp differences.

Sometimes it is desired to compare the effects of factors, such as loom speed, that can conveniently be varied during the weaving of each piece of cloth without disturbing the general set-up of the warp and loom. Then the



between-piece variance does not contribute to the errors of the comparisons, which are consequently much reduced. Frequently it is possible to combine the investigation of such factors with that of factors involving the sizing of separate warps by adopting an arrangement analogous to the "split-plots" used in agricultural experiments. Suppose, for example, the additional factor is loom speed which is adjusted to three values. Then one-third of each piece is woven at each speed, and the results make it possible to measure and test the significance of (1) the average difference between the warps, (2) the average effect of loom speed and (3) the so-called "interaction" between loom speed and warps, i.e. the extent to which the effect of loom speed varies for the different warps. Since the within-piece variance is comparatively small, the effect of loom speed is measured with comparatively great precision, and it may be thought desirable to include still more factors that can be varied within a piece, varying different factors on different pieces and "confounding" some of the higher order interactions. There are, however, objections to making experiments unduly complicated, and these arise from considerations which will be mentioned later (p. T218).

#### Most Economical Piece Length

From equation (1) or (2), with some additional information, it is possible to work out the most economical piece-length for a given size of experiment, and hence the most economical number of interchanges. Let the cost to weave 10,000 picks of a given cloth be  $w$  and the cost to perform an interchange on one warp be  $iw$ . These costs should include wages, overhead costs and (theoretically) more intangible costs such as the effect of delay at the interchange. Then if the total cost to weave a piece of cloth is  $C$ ,

$$C = (i + N)w$$

where  $N$  is again the number of units of 10,000 picks in a piece. The most economical experiment will be one in which for a given error variance the cost per piece is a minimum; or alternatively for a given cost per piece the error variance is a minimum; i.e. the quantity (variance  $\times$  cost per piece) should be a minimum. Now

$$VC = (c + \frac{h}{N})(i + N)wB,$$

and on differentiating this with respect to  $N$  and equating to zero the following result is obtained.—

$$N^2 = \frac{ih}{c} = 7 \cdot 5i \text{ [from equation (2)]} \quad \dots \quad (3)$$

For the following cloth:

Florentine drill; 29½"; 96  $\times$  56; 20/18,

it has been calculated that  $i$  is approximately 20 under the conditions obtaining at the Institute, so that from equation (3)  $N^2 = 150$ ,  $N$  is about 12 and the corresponding piece-length is about 60 yards. For another cloth:

Poplin, 37", 144  $\times$  76, 50/50,

$i$  is approximately 40,  $N^2$  is 300 and the piece-length is again 60 yards. For the Florentine cloth, at  $N = 12$ ,  $VC = 10 \cdot 4 wB$ ; if  $N$  is increased to 18, corresponding to 90 yards of cloth per piece,  $VC$  is only increased to  $10 \cdot 7 wB$ . Hence the efficiency of the experiment is not much reduced by fairly large deviations from the optimum in piece-length. In view of this, of the fact that the optimum of 60 yards applies to two very different cloths, and also of the roughness with which  $i$  is estimated, any piece-length of the order of

50-100 yards is reasonably economical. This is fortunate, for such lengths are technically convenient, particularly in sizing.

#### Standard Error of Mean Breakage Rate

Equation (2) leads directly to an expression for the standard error of the mean breakage rate of a warp when comparing it with the breakage rate of another, provided both warps are woven in the same experiment arranged in randomised blocks or a Latin square. If  $M$  is the number of pieces per warp,

$$\text{Standard error} = \sqrt{\frac{V}{M}} = \sqrt{\left(\frac{1}{5} + \frac{3}{2N}\right) \frac{B}{M}} \quad \dots (4)$$

Equation (4) can be used for deciding on what scale it is necessary to do a given experiment provided the required precision is given. For example, suppose that for the Florentine drill referred to on p.116  $B$  averages 1.8 and 80-yard pieces are woven so that  $N=16$ . If it is desired to measure breakage rates of warps with a precision such that a difference of 0.5 breaks per 10,000 picks is significant at the 5 per cent level then  $2\sqrt{2} \times \text{standard error} = 0.5$  and the standard error is 0.177. When these values are substituted and equation (4) is solved for  $M$ ,  $M=17$ ; i.e. there should be 17 pieces per "warp", and this will involve putting the yarn on two beams. It is quite clear that for this cloth a single  $4 \times 4$  Latin square experiment gives a result of very low precision.

When comparisons are made between treatments that are varied during the weaving of the same piece of cloth without disturbing the gait-up of the loom, the standard error may be obtained from equation (4) as

$$\text{Standard error} = \sqrt{\frac{3B}{2N'}} \dots \dots \dots (5)$$

where  $N'$  is the total number of 10,000-pick units woven with each treatment.

The question arises whether it is legitimate to use equations (2), (4) and (5) to estimate the error in any particular experiment instead of estimating the variance directly from the data. There is a great temptation to do so, for a considerable increase in efficiency of the experiment results. In order to estimate this increase, we will suppose we are interested in testing the significance of the difference between two warps in a  $4 \times 4$  randomised block experiment. In such an experiment, the error variance is estimated on 9 degrees of freedom and  $t=2.262$  lies on the 5 per cent. level of significance, if equation (2) or one of its derivatives could legitimately be applied, the error variance would be estimated on the equivalent of an infinite number of degrees of freedom and  $t=1.960$  would lie on the 5 per cent level. To make a given difference in warp means just significant on the 5 per cent level, the second method would require a smaller number of pieces to be woven than the first, in the ratio of 1 to  $(2.262)^2/(1.960)^2$ , i.e. 1 to 1.33 or 3 to 4. At the 1 per cent level of significance this ratio is 1 to  $(3.250)^2/(2.576)^2 = 1$  to 1.59. The gain in experimental efficiency by using the equations for obtaining the error is substantial, but considerable caution is necessary in following such a course of action. The investigator will need to satisfy himself that the general conditions under which equation (1), and its approximation equation (2) arose still obtain in his experiment, e.g. that there has been no change in technique or variability of materials, and he must be on the look-out for evidence of exceptionally high variations in particular instances. In doing this, he must also be careful he does not

drift into the habit of using equation (2) when it gives the smaller of the two measures of variance and the direct estimate when that gives the smaller one.

#### The Use of a Transformation of the Variable

The tests of significance derived from the analysis of variance are based on the assumption that the error variance is the same for all looms and experimental treatments. The results summarised in equation (2) show that in general this cannot be true. In any one experiment, the average breakage rate will tend to be different on the different looms, and a loom with a high breakage rate will also have a high error variance. It has been suggested that this difficulty may be largely overcome by making the transformation  $u = \sqrt{b}$ , where  $b$  is the breakage rate for each piece, and analysing the variance of the value of  $u$ . Where the variance of  $b$  is proportional to the mean value,  $B$ , as in equation (2), that of  $u$  is practically independent of the mean value of  $u$  and the ordinary technique of analysis of variance is valid<sup>\*</sup>. In most straightforward weaving experiments with one factor varied, however, as in the example given in full in an earlier section, the loom effect is not large enough to make the transformation necessary, and the same conclusions are usually reached whether the analysis is of the transformed or untransformed variable. In a complex experiment where two factors are investigated, on the other hand, a transformation may be desirable to make the tests of significance valid, but it may make the technical interpretation of the results difficult. Suppose in the example on p. 7216 there are large real differences between warps, between speeds and between looms\*. Then the analysis of variance of the untransformed breakage rates does not give a valid estimate of error against which to test the interaction effect, but the significance of the interaction measured in terms of the transformed variable may or may not correspond to its significance in terms of warp breaks. The following hypothetical conditions illustrate this difficulty. (1) For a number of warps differing in breakage rate, the change in warp breaks for a given change in speed might be on the average the same for all warps, the change in  $\sqrt{\text{warp breaks}}$  would then be greater for warps with low than for those with high breakage rates. (2) The change in breakage rate with speed might be small for warps of low breakage rate and so much larger for warps of high breakage rate as to make the changes in  $\sqrt{\text{warp breaks}}$  substantially the same for all warps. The first of these conditions might result in a significant interaction for  $\sqrt{\text{warp breaks}}$  although for the untransformed warp breaks there would actually be no interaction; and the second condition might not give a significant interaction for  $\sqrt{\text{warp breaks}}$  although there would be a real interaction for the untransformed warp breaks. It would not, however, be safe to infer an interaction for warp breaks from an absence of interaction for  $\sqrt{\text{warp breaks}}$  or vice versa. For technical purposes, it is of course necessary to present and interpret all results in terms of warp breaks, and owing to the difficulty of doing this when the analysis is performed on the transformed data, it is desirable to avoid the need for the transformation, either by keeping the experiment fairly simple, or by using a complex design only in preliminary experiments designed to show qualitatively what treatments and interactions are likely to have large effects, or in experiments where the effects of the factors are relatively small.

---

\* This supposition is made purely for the sake of an example. It is not suggested that in fact loom speed affects the warp breakage rate.

### **Effects of Interactions on the Design and the Scale of Replication**

In the foregoing discussion, the errors estimated have been mostly of the relative mean breakage rates for the several *warps* in an experiment, each warp representing one experimental treatment. It is the treatment effect that is, of course, of interest, and this is not necessarily exactly the same as the warp effect. If the experiment were repeated several times, each replication being made from the beginning, on a different batch of yarn sized on a separate occasion, it is probable that the results for the several experiments would differ by more than would be expected from the error within an experiment, as measured by  $V$ , equation (2), i.e. that lack of control in the preparation of the warps would add to the errors. No estimate has yet been made of these additional errors, they have been assumed to be small and as a check, regard has been paid to the internal consistency of the results—i.e. the extent to which the breakage rates for a natural sequence of treatments also follow a sequence. A sound arrangement would be one in which a Latin square or randomised block scheme was used, each piece being prepared separately. Unfortunately the processes of warp preparation, particularly sizing, do not lend themselves to the independent preparation of short lengths of yarn and as a compromise, experiments are now being done in duplicate, a repetition being made of the sizing, mostly with separate yarn deliveries. When enough data have been obtained, it will be possible to estimate the additional preparation errors, add a corresponding term to equation (2) and work out the most economical number of pieces per warp having due regard to the costs and technical limitations of preparation.

In repeating such experiments, it is necessary to consider what factors should be allowed to vary between replicates. For example, suppose it is desired to measure the effect on weaving breaks of the amount of size on the warp and to determine the best amount. The effect will depend on the cloth particulars, and may also depend on say (1) the quality of yarn used, (2) the kind and set-up of the looms, (3) the relative humidity of the atmosphere of the weaving shed and (4) the quality and proportion of the sizing ingredients used. These may be called *subsidiary* factors. A simple experiment done under well-controlled conditions will establish results that apply with a known precision to other warps of that cloth woven from that particular quality of yarn in these looms at the given humidity, when using the particular sizing ingredients. Such results are of little practical use, however; they need to have a much wider range of application. Results applying to one cloth may be useful enough, if the cloth is one that is commonly woven; and it is possible to specify a single size mixing that many, if not most, manufacturers would use. Any one manufacturer might also be content with results applying to one quality of yarn, make of loom, and quality of sizing ingredients, provided these were used by him; but deliveries of yarn and sizing ingredients of the same nominal quality differ, overlookers in the mill do not all set up their looms in quite the same way, and the relative humidity of the atmosphere is not usually controlled with accuracy, so that it would be desirable to introduce variations in these subsidiary factors into the replicates of the experiment. A central institution like the Shirley Institute requires, however, to generalise the results for the use of many manufacturers, and ideally the replicate experiments should sample the full range of qualities of yarns and sizing ingredients that would

be used for the cloth, and should be done in several kinds of looms at several humidities. In an ideally complete set of experiments, each of the subsidiary factors would be represented at say three or four values or "levels" and one experiment would be done at each combination of the levels of the four subsidiary factors. This would make possible a determination of the effects of all the factors and their various interactions, but would involve working on an impossibly large scale.

Even if the interactions between the subsidiary factors were neglected, it would require a very large set of experiments to determine their interaction with the main effect under investigation—that of the amount of size on the warp. In fact, it is not practicable to repeat the experiment more than two or three times, and in the circumstances it is desirable that each repetition should be done with a different value of all the subsidiary factors. Then the effects of these factors cannot be measured and their interaction with the main effects adds to the error with which that effect is determined; but a valid estimate is made of the error with which the results may be widely applied to the various qualities of yarn, types of loom, etc. It is desirable, of course, that in the factory all important factors should be controlled as closely as possible to the best values.

In designing an actual experiment, the principles just illustrated are borne well in mind, but practical difficulties also have their influence. It is not convenient to vary some subsidiary factors in replicating experiments and if it is considered unlikely that these factors will have any important interaction with the main factor they are kept constant. Some subsidiary factors may be kept constant even though their interaction with the main factor may not be negligible, because it is extremely difficult to vary them. For example, experiments at the Institute can only be done on the particular looms available, run by the particular weavers and overlookers employed, and it is not easy to arrange for a varied atmospheric humidity. Results are obtained under these conditions, and an estimate, based on general experience, is made of how far the results are likely to apply under mill conditions.

#### REFERENCES

- <sup>1</sup> Tippett *Shirley Inst. Mem.*, 1929, 8, 175, or *J. Text. Inst.*, 1930, 21, T105
- <sup>2</sup> Tippett *Shirley Inst. Mem.*, 1934, 13, 35, or *J. Text. Inst.*, 1935, 26, T13
- <sup>3</sup> Tippett *Shirley Inst. Mem.*, 1934, 13, 61, or *J. Text. Inst.*, 1935, 26, T51

# THE JOURNAL OF THE TEXTILE INSTITUTE

## TRANSACTIONS

### 19—AN EXAMINATION OF THE RELATION BETWEEN WOOL QUALITY AND FIBRE DIAMETER

By J L STOVES, Ph D.

*Copyright by the Textile Institute*

#### I. HISTORICAL

It was not until the discovery of the microscope that attention was paid to the structure of wool. One of the earliest observations is that of Dr Hooke, who examined wool and hair under the microscope. His findings are described in a paper to the Royal Society, London, a complete account appearing in "Micrographia of some Physiological Descriptions of Minute Bodies made by Magnifying Glasses, with observations and inquiries thereupon," London, John Martyn, 1665. Some years later, Leeuwenhoeck<sup>1</sup> stated that "the wool fibre is a hard exterior tube with medulla or pith within." This preliminary work, together with that of Baker,<sup>2</sup> paved the way for the quantitative examinations of Daubenton, who published a series of papers from 1777 to 1784 upon sheep and wool. He advocated the use of the microscope for assessing the fineness of wool and discussed the question of the significance of wool fineness in relation to its manufacturing properties. Reasons for the fixation of different fineness grades of wool were given as:—

(1) To avoid uncertainty in commercial relations.

(2) For the proper ascertainment of breeding results

From that time until the present, the problem of the relation between fibre fineness and wool quality has received attention in this country and on the Continent. Especially during the last twenty years has extensive research in the wool industry been carried out. The works of Kronacher<sup>3</sup> and Barker<sup>4</sup> summarise developments to 1930.

#### II. FIBRE FINENESS AND WOOL QUALITY

An early attempt to correlate fibre fineness and wool quality was made by Holden<sup>5</sup>, who determined the relationship between fibre diameter and English quality number on a series of tops. Forty fibres of each quality were selected from commercial standard tops and five measurements were made on each individual fibre. His conclusions were as follows:—"From the results it would seem that a basis exists for a standard of fibre thickness which will correspond to quality numbers, and this affords some indication of the approximate diameter to which each quality in the range should be expected to conform."

A summary of his results is given in Table I.

Table I

Quality ...	80's	70's	64's	60's	58's	56's	54's	50's	48's	46's	40's	36's
Fibre diameter (microns)	20.1	21.9	24.5	25.6	26.6	27.8	29.4	32.0	34.0	36.6	42.0	45.2

Six years later, as a result of work on standards of thickness, Duerden<sup>6</sup> published results of microscopic measurements of fibre diameter of wool samples graded by an experienced sorter. His scale for standard quality numbers and their corresponding mean diameters is given in Table II.

Table II

Quality	100's	90's	80's	70's	64's	60's	58's	56's	54's
Fibre diameter (microns)	15-16	16-17	17-18	18-19	20-22	22-24	24-26	26-28	28-32

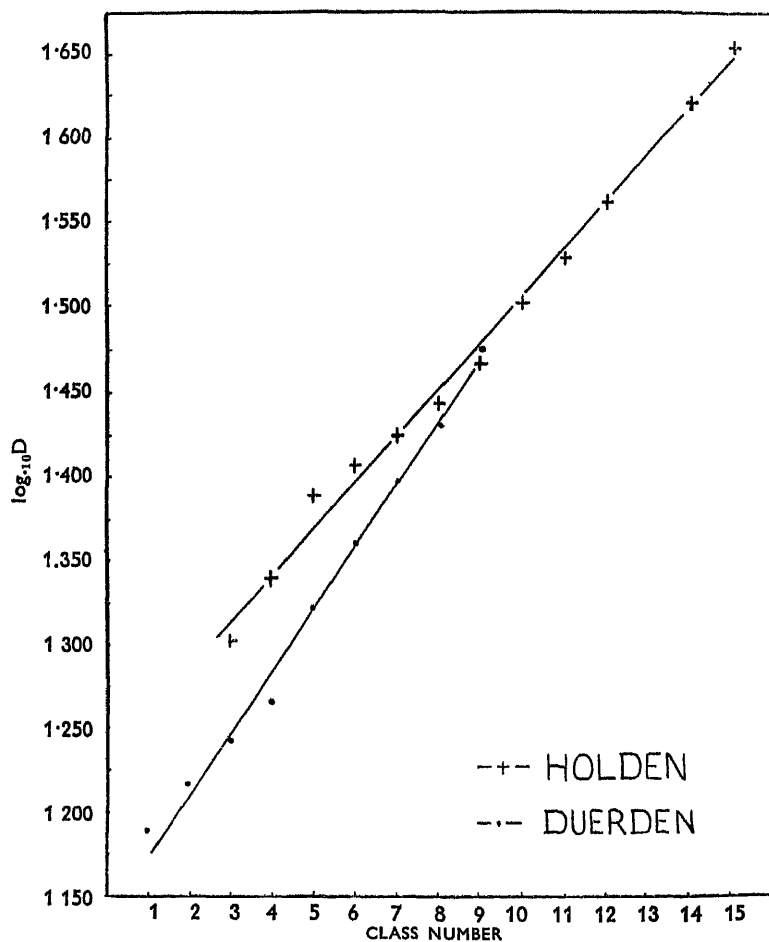


Fig. 1

Fig. 1 illustrates these two sets of results,  $\log_{10} D$  being plotted against Quality Numbers which are spaced at equal intervals and termed Class 1, 2, 3 . . .

On the basis of Duerden's work, Oliver<sup>7</sup> suggested a new scale for wool quality, such that commencing at 56's, grades would advance in arithmetic progression.

In 1931, Barker and Winson<sup>8</sup> found that a linear relationship existed between the logarithm of fineness of a top, expressed as the weight in mgm

of 10 metres of fibre at 18.25 per cent regain, and its position in the quality scale, when equal intervals were taken between qualities. A similar relationship was demonstrated for standard top in French, German and Italian notations, so proving that the fundamental basis underlying wool sorting is the same in all countries. The basic principle common to all sorting methods is expressed in the Fechner-Weber psycho-physical law, which states:—"In order that the intensity of a sensation may increase in arithmetical progression, the stimulus must increase in geometrical progression."

Theoretically, Barker and Winson's gravimetric method of determining fibre diameter is the best, but the practical application is limited to raw wool and top, and can only be used for non-medullated wools. For factory work the width measurement has the advantage of being the simplest and quickest to perform, while for the purpose of classification without regard to spinning properties of the wool, the method is quite reliable.<sup>9</sup>

Assuming a circular cross-section for the wool fibre, it is possible to calculate the fibre diameter from the expression:—

$$D = 2 \times \sqrt{\frac{W}{\Delta \pi L}}$$

where  $W$  is the weight of a fibre of length  $L$  and density  $\Delta$ .<sup>\*</sup> Table III contains such theoretical values of fibre diameter calculated from the gravimetric results of Barker and Winson. Values of fibre fineness computed from cross-sectional measurements are also included.

Table III  
Fibre diameter (microns)

Quality	80's	70's	64's	60's	58's	56's	50's	48's	46's	44's	40's	36's
(a) Gravimetric	19.6	20.4	22.3	24.3	25.7	28.1	31.1	32.9	—	—	—	—
(b) Cross-sectional	19.2	20.7	21.4	24.4	26.0	27.7	31.5	33.8	35.1	37.6	38.2	39.0

Winson<sup>10</sup> stressed the importance of fibre fineness in determining wool quality, and suggested that while other characteristics such as length, crimp, elasticity and lustre are of decided importance in assessing the manufacturing values of a sample of wool, yet it is only in so far as these properties are present to an abnormal degree that an evaluation of quality based on fineness alone is called into question.

Unlike the results of Holden, those of Barker and Winson do not exhibit a linear relationship between Quality Number and the logarithm of fibre fineness in wools below 48's quality. In the case of the gravimetric method of fineness measurement, the presence of medullated fibres invalidates results at the lower end of the scale, but even for the cross-sectional area values the same deviation from the Fechner-Weber Law occurs.

This anomaly was also observed by von Bergen<sup>11</sup>. Using the Wedge Method of direct measurement, he compiled a set of values which is reproduced in Table IV, illustrated by Fig. 3.

Table IV

Quality	80's	70's	64's	60's	58's	56's	50's	48's	46's	44's	40's	36's
Fibre diameter (microns)	19.5	20.8	21.9	23.5	24.8	27.0	30.4	33.0	34.8	36.6	38.3	39.8

\* See Addendum



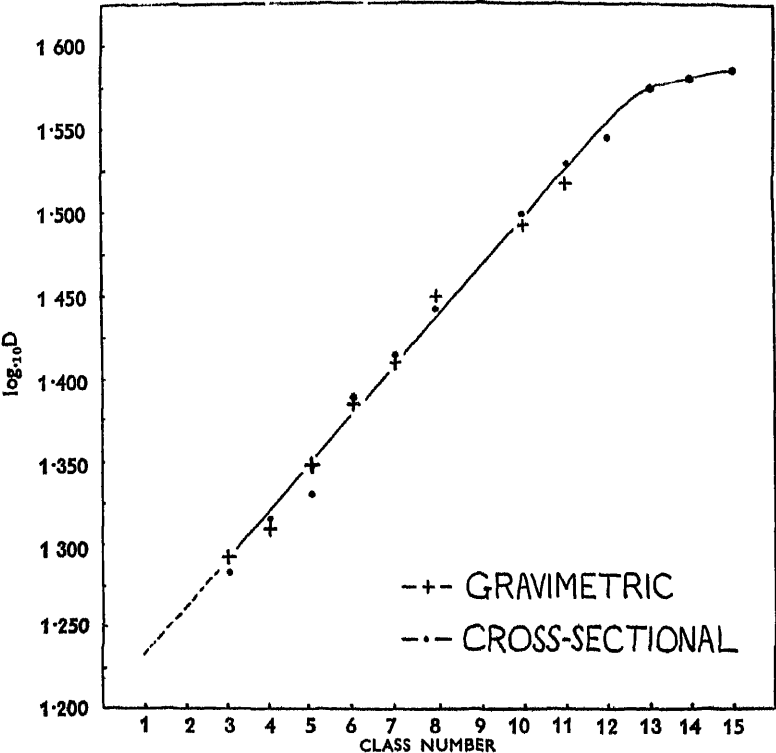
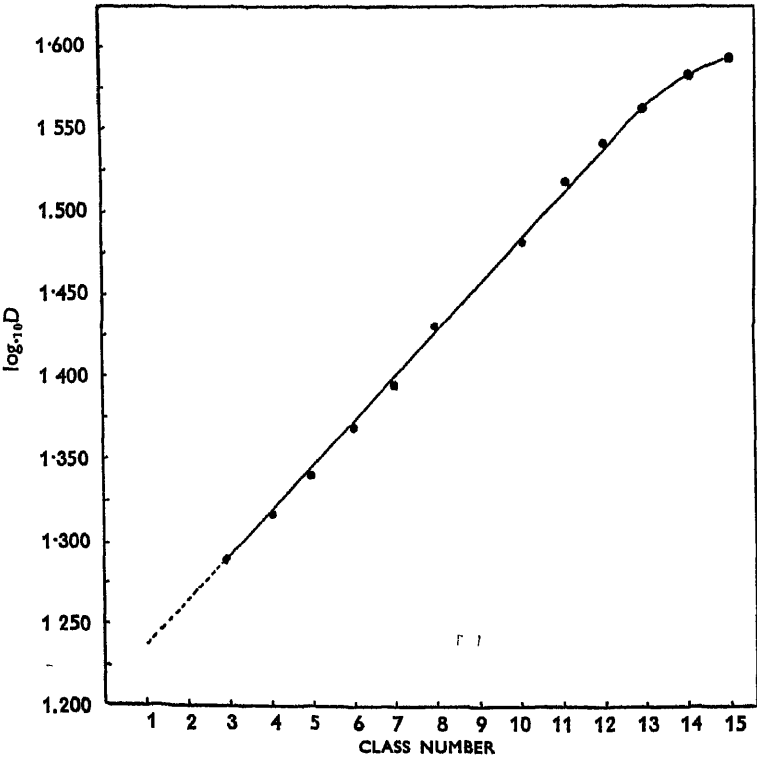


Fig. 2



The means of the theoretical values of  $\log_{10} D$  obtained from curves 2 and 3 are related to Class Number ( $N$ ) by the expression:—

$$N = 34.82 \log_{10} D - 41.93$$

$D$  being measured in microns.

Using these theoretical values of  $\log_{10} D$ , it has been possible to construct a modified table showing the relation between fibre fineness and quality number (Table V).

Table V

Class No	...	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Quality	...	100's	90's	80's	70's	64's	60's	58's	56's	54's	50's	48's	46's	44's	40's	36's
Fibre diam (microns)		17.1	18.3	19.6	20.8	22.3	23.9	25.5	27.2	29.0	31.0	33.1	35.5	37.2	38.3	39.2

At present, there is no official table correlating fibre diameter and wool quality, and the widely differing values to be found in the literature recently proved to be a serious disadvantage when the author was called upon to check wool quality numbers by means of fibre fineness measurements. It is for this reason that the present survey of the literature has been made, and the above results deduced. Table V, therefore, may prove of value to microscopists using fineness measurements as a check upon wool quality, especially in cases of classification without regard to spinning properties.

The importance of the relation between fibre fineness and quality number has been pointed out by Kershaw<sup>12</sup> in a communication stressing the value of education for quality consciousness. Wilsdon,<sup>13</sup> however, in referring to proposals made by Bernhardt<sup>14</sup> for the establishing of a definitive relationship between measurements of wool fineness and accepted designations of wool quality, pointed out the decision of the International Wool Textile Organisation<sup>15</sup> that it was undesirable in view of the many separate characteristics which enter into the assessment of quality and the arbitrary nature of conventional grades, to place wool quality and fineness into direct relation with one another. Unavoidable sampling and experimental errors make it advisable to avoid any system of differentiation based on rigid grade boundaries. It was also decided that any satisfactory type of apparatus would be recognised for measuring fineness in cases of arbitration.

An explanation of these apparently divergent views is found in the fact that while wool sorting is based on fibre fineness, the subsequent manufacturing performance of the wool may involve other factors, spinning property being a combination of fineness, adequate length and other characteristics of the fibre. This view has been expressed recently by Wilson<sup>16</sup>, who states: "Wool of 60's quality should spin 60 × 560 yds/lb. This, however, does not hold true, as most wools will not spin to their quality numbers. The quality number was originally based upon the fibre diameter and to-day is the main feature upon which we judge quality, though many other factors play an important part in the actual spinning properties of the fibres . . . The commercial value is decided not only upon the diameter of the fibres, but also on such properties as length, waviness, uniformity, strength, elasticity, etc."

### III. METHODS OF MEASUREMENT

As regards the measurement of wool fineness, a definite decision was reached in 1936.<sup>17</sup> Four 2 mm sections are cut from top or yarn, the sections being shaken up in cedar-wood oil to ensure mixing, and the diameters of

two samples of 200 fibres (300 for crossbred wool) are determined by means of a projection microscope with a magnification of 500.

Two years later, however, Daniels<sup>18</sup> drew attention to the following potential sources of experimental error in the standard method of fineness measurement: (1) humidity of atmosphere, (2) water content of cedar-wood oil used, (3) drawback of the method of allowing fibres to settle before sampling, (4) necessity of cutting fibres as short as possible to obviate the tendency for felting to occur, (5) differences between measurements made by different observers.

About the same period, Henning<sup>19</sup> brought forward results of a statistical treatment of fibre diameter measurements. The percentage standard error for merinos and crossbreds was found to increase steadily with mean fineness. The percentage standard error of merino quality lies between 1.48 per cent. for mean fineness of  $16\mu$  and 1.87 per cent. for mean fineness of  $25\mu$  (200 individual measurements), while for crossbreds the values are 1.53 per cent. for  $25\mu$  and 1.71 per cent. for  $36\mu$  (300 measurements). If, however, 300 measurements are made for merinos and 600 for crossbreds, the standard error is between 1.21-1.53 per cent. for merinos ( $16-25\mu$ ), and between 1.08-1.21 per cent. for crossbreds ( $25-36\mu$ ).

The author thanks the Directors of C. W. Martin & Sons, Ltd, for permission to publish this paper.

#### ADDENDUM\*

The value of  $D$  obtained from the expression:—

$$D = 2 \times \sqrt{\frac{W}{\Delta\pi L}}$$

is the root-mean-squared fibre diameter, and is related to the mean diameter  $D_w$ , as determined by the width method, by the formula —

$$D = \sqrt{D_w^2 + \sigma_w^2} = D_w \sqrt{1 + v^2}$$

where  $\sigma_w$  is the standard deviation of the distribution of fibre width measurements, and  $v = \sigma_w/D_w$ .

Since the value of  $v$  is generally about 0.25, it follows that  $D$  will exceed  $D_w$  by about 3 per cent. The same remark applies to the mean diameter calculated from cross-sectional areas.

#### REFERENCES

- <sup>1</sup> Leeuwenhoeck. *Phil Trans Roy Soc*, London, 1678, 12, 1004.
- <sup>2</sup> H. Baker. "The Microscope Made Easy" 1754. Ch. 44.
- <sup>3</sup> C. Kronacher and A. Lodemann. *Technik der Haar- und Wolleuntersuchung*, Berlin, 1930.
- <sup>4</sup> S. G. Barker. "Wool Quality," London, 1931.
- <sup>5</sup> H. S. Holden. *J. Text. Inst.*, 1922, 13, 1157.
- <sup>6</sup> J. E. Duerden. *Wool Record*, 1928, 34, 571.
- <sup>7</sup> T. Oliver. *J. Text. Inst.*, 1929, 20, 1218.
- <sup>8</sup> S. G. Barker and C. G. Winson. *J. Text. Inst.*, 1931, 22, 1314.
- <sup>9</sup> S. G. Barker and A. T. King. *J. Text. Inst.*, 1926, 17, 168.
- <sup>10</sup> C. G. Winson. *J. Text. Inst.*, 1931, 22, 1533.
- <sup>11</sup> W. von Bergen. *Proc. Amer. Soc. for Testing Materials*, 1935, 35, 14.
- <sup>12</sup> S. Kershaw. *J. Text. Inst.*, 1938, 29, 304.
- <sup>13</sup> B. H. Wilsdon. *Textilber.*, 1938, 19, 777, No. 4E, 161.
- <sup>14</sup> Beinhart. *Textilber.*, 1938, 19, 11-13.
- <sup>15</sup> Int. Wool Textile Organisation, London Conference, June, 1938.
- <sup>16</sup> D. Wilson. *J. Text. Inst.*, 1940, 31, 24.
- <sup>17</sup> H. Rausch. *Proc. 12th Int. Wool Conf.*, 1936, p. 22.
- <sup>18</sup> H. E. Daniels. *14th Int. Wool Conf.*, 1938, *Tech. Comm. Proc.*, p. 64.
- <sup>19</sup> H. J. Henning. *14th Int. Wool Conf.*, 1938, *Tech. Comm. Proc.*, p. 66.

# THE Journal of the Textile Institute

VOL. XXXII—1941

## TRANSACTIONS—NAME INDEX

	PAGE		PAGE
<b>B</b>		<b>H</b>	
Brownsett, T, and Clibbens, D A Comparison of the Rates of Flow of Modified Cotton Celluloses Dissolved in Solutions of Trimethylbenzylammonium Hydroxide (Triton B), Dimethyldibenzylammonium Hydroxide (Triton F), Sodium Hydroxide, Cuprammonium and Cupriethylenediamine	T57	Hancock, H A, and Dunkerley, F Relative Yarn Strengths using Casablancas and Three-line Draft Systems at the Speed Frame	T193
" and Clibbens, D A Dissolution of Chemically Modified Cotton Cellulose in Alkaline Solutions Part VII The Solvent Action of Solutions of Trimethylbenzyl- and Dimethyldibenzyl-ammonium Hydroxides (Triton B and F)	T25	Howitt, F O, <i>see</i> Cadwallader, C J	T13
" and Davidson, G F Dissolution of Chemically Modified Cotton Cellulose on Alkaline Solutions Part VI Effect of Method of Modification on the Relation between Fractional Solubility in Sodium Hydroxide Solutions and Fluidity in Cuprammonium Solution	T25	" <i>see</i> Garrett, C H	T1
<b>C</b>		<b>J</b>	
Cadwallader, C J, Howitt, F O, and Smith, S G Fluidity of Silk Solutions Part II Application	T13	Jambuserwala, G B Modified Starches Part IV Action of Alkalis on Starches	T101
Clibbens, D A, <i>see</i> Brownsett, T	T32, T57	<b>L</b>	
<b>D</b>		Larose, P Breaking Strength of Fabrics	T167
Davidson, G F, <i>see</i> Brownsett, T	T25	<b>M</b>	
" Progressive Oxidation of Cotton Cellulose by Chromic Acid over a Wide Range of Oxygen Consumption	T132	Macmillan, W G, and Sen, M K Comparative Observations on the Swelling of Jute Fibre .2—Specific Gravity and Swelling	T45
" Progressive Oxidation of Cotton Cellulose by Periodic Acid and Metaperiodate over a Wide Range of Oxygen Consumption	T109	Mam, V R, and Tippett, L H C Statistical Methods in Textile Research Part IV—The Design of Weaving Experiments	T209
Dunkerley, F, <i>see</i> Hancock, H A	T193	Martindale, J G Correlation Periodograph for the Measurement of Periods in Disturbed Wave-Forms	T71
" Roller Settings and Yarn Strengths	T179	<b>R</b>	
" Yarn Strengths of Egyptian Mixings Three-line Roller Systems	T197	Rees, W H Transmission of Heat through Textile Fabrics	T149
<b>G</b>		<b>S</b>	
Garrett, C H, and Howitt, F O Fluidity of Silk Solutions Part I—Measurement	T1	Sen, M K, <i>see</i> Macmillan, W G	T45
		Smith, S G, <i>see</i> Cadwallader, C J	T13
		Speakman, J B Mather Lecture—The Chemistry of Wool and Related Fibres	T83
		Stoves, J L Examination of the Relation between Wool Quality and Fibre Diameter	T221
		<b>T</b>	
		Tippett, L H C, <i>see</i> Mam, V R	T209



# TRANSACTIONS—SUBJECT INDEX

	PAGE		PAGE
<b>B</b>		<b>M</b>	
Breaking Strength of Fabrics P Larose	T167	Mather Lecture The Chemistry of Wool and Related Fibres J B Speakman	T81
Comparison of the Rates of Flow of Modified Cotton Celluloses dissolved in Solutions of Trimethylbenzylammonium Hydroxide (Triton B), Dimethylbenzylammonium Hydroxide (Triton F), Sodium Hydroxide, Cuprammonium and Cupriethylenediamine T Brownsett and D A Clibbens	T57	Modified Starches Part IV—Action of Alkalis on Starches. G B. Jambuserwala	T206
Comparative Observations on the Swelling of Jute Fibre 2—Specific Gravity and Swelling W. G Macmillan and M K Sen	T45	<b>P</b>	
Distortion Periodograph for the Measurement of Periods in Disturbed Wave-Forms J G Martindale	T71	Progressive Oxidation of Cotton Cellulose by Chromic Acid over a Wide Range of Oxygen Consumption G F Davidson	T132
<b>D</b>		Progressive Oxidation of Cotton Cellulose by Periodic Acid and Metaperiodate over a Wide Range of Oxygen Consumption G F. Davidson	T109
Dissolution of Chemically Modified Cotton Cellulose in Alkaline Solutions Part VI—Effect of Method of Modification on the Relation between Fractional Solubility in Sodium Hydroxide Solution and Fluidity in Cuprammonium Solution T Brownsett and G F Davidson	T25	<b>R</b>	
Dissolution of Chemically Modified Cotton Cellulose in Alkaline Solutions Part VII—The Solvent Action of Solutions of Trimethylbenzyl and Dimethylbenzylammonium Hydroxides (Tritons Band F) T Brownsett and D A Clibbens	T32	Relative Yarn Strengths using Casablanca and Threeline Draft Systems at the Speed Frames H A Hancock and F Dunkerley	T193
<b>E</b>		Roller Settings and Yarn Strengths F Dunkerley	T179
Examination of the Relation between Wool Quality and Fibre Diameter. J. L. Stoves	T221	<b>S</b>	
Fluidity of Silk Solutions Part I—Measurement C H Garrett and F O. Howitt	T11	Statistical Methods in Textile Research Part IV.—The Design of Weaving Experiments V R Main and L H C Tippet	T209
Fluidity of Silk Solutions Part II—Application C J Cadwallader, F O Howitt, and S G Smith	T13	<b>T</b>	
<b>Du</b>		Transmission of Heat through Textile Fabrics W. H. Rees	T149
		<b>Y</b>	
		Yarn Strengths of Egyptian Mixings Three line Roller Systems F. Dunkerley	T197



**Indian Agricultural Research Institute (Pusa)**  
LIBRARY, NEW DELHI-110012

This book can be issued on or before .....

Return Date	Return Date